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(71) Applicant: SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V. [NL/NL]; Carel van Bylandtlaan 30, NL–2596 HR The Hague (NL).

(72) Inventors: KRAVETZ, Louis; 4926 Gleneagles Drive, Houston, TX 77084 (US). MURRAY, Brendan, Dermot; 1118 Stoneyhill Drive, Houston, TX 77077 (US). SINGLETON, David, Michael; 12622 Rocky Meadow Drive, Houston, TX 77024 (US).

(54) Title: HIGHLY BRANCHED PRIMARY ALCOHOL COMPOSITIONS, AND BIODEGRADABLE DETERGENTS MADE THEREFROM

(57) Abstract

There is provided a new branched primary alcohol composition and the sulfates, alkoxylates, alkoxy sulfates and carboxylates thereof exhibiting good cold water detergency and biodegradability. The branched primary alcohol composition has an average number of branches per chain of 0.7 to 3.0, having at least 8 carbon atoms and containing both methyl and ethyl branches. The primary alcohol composition may also contain less than 0.5 atom% of quaternary carbon atoms, and a significant number of ethyl branches, terminal isopropyl branches, and branching at the C_3 position relative to the hydroxyl carbon. The process for its manufacture is by skeletally isomerizing an olefin feed having at least 7 carbon atoms or by dimerising a C_6–C_{10} olefin, followed by conversion to an alcohol, as by way of hydroformylation, and ultimately sulfation, alkoxylation or both to obtain a detergent surfactant. Useful skeletal isomerization catalysts include the zeolites having at least one channel with a crystallographic free diameter along the x and/or y planes of the [001] view ranging from 42 to 70 nanometer. Useful dimerisation catalysts include a combination of a nickel carboxylate with an alkyl aluminium halids, or a combination of a nickel chelate with an alkyl aluminium alkoxide.

HIGHLY BRANCHED PRIMARY ALCOHOL COMPOSITIONS, AND
BIODEGRADABLE DETERGENTS MADE THEREFROM

1. Field of the Invention

The invention pertains to a new primary alcohol
composition and the alkoxylates, sulfates and alkoxy
sulfates thereof and to their production and uses.

2. Background of the Invention

The alcohols of long chain olefins, especially those
having about 10 to 28 carbon atoms, have considerable
commercial importance in a variety of applications
including detergents, soaps, surfactants, and freeze
point depressants in lubricating oils. These alcohols are
produced by any one of commercial processes, such as the
oxo or hydroformylation of long chain olefins. Typical
long chain alcohols are the commercially available NEODOL
alcohols made by Shell Chemical Company, the EXXAL
alcohols available from Exxon Chemical, and the LIAL
alcohols available from Enichem (NEODOL, EXXAL and LIAL
are trade marks).

In the manufacture of the NEODOL alcohols, a pre-
dominantly linear olefin feed is subjected to hydro-
formylation by reacting carbon monoxide and hydrogen onto
the olefin in the presence of an Oxo catalyst to form an
alcohol. In excess of 80% of the number of alcohol
molecules in the resultant alcohol composition are linear
primary alcohols. Of the branched primary alcohols in
the composition, substantially all, if not all, of the
branching is on the C_2 carbon atom relative to the hydro-
xyl bearing carbon atom. These alcohols can subsequently
be converted to anionic or nonionic detergents or general

surfactants by sulfonation or ethoxylation, respectively,
of the alcohol. Also known as anionic surfactants for
detergents are the alcohol-ethoxysulfates.

The NEODOL line of alcohols has met with considerable
commercial success with detergents because the NEODOL
alcohol compositions can be economically produced with
high yields of linear alcohols. The desire to use linear
alcohols as intermediates for detergent grade surfactants
exists because it is generally recognized that linear
alcohols biodegrade, while the branched long chain
alcohol sulfonates exhibit poor biodegradability. Since
detergents and soaps used by consumers for washing are
ultimately released into the environment, the need to
provide a surfactant or detergent which biodegrades is
well recognized.

For example, US 5,112,519 describes the manufacture
of a surfactant by oligomerizing C_3 and C_4 olefins
through a surface deactivated ZSM-23 catalyst to form
oligomers, hydroformylating the oligomer, and recovering
a semi-linear alcohol composition having less than
1.4 methyl branches, and whose branching is limited to
methyl branches. The alcohol can be ethoxylated and/or
sulfated and is reported to be biodegradable, and further
have improved low temperature properties compared to iso-
tridecyl alcohol. Retaining the linearity of the alcohol
composition to less than 1.4, along with obtaining
methyl branching were important considerations to
achieving a biodegradable surfactant. It would be
desirable, however, to obtain a biodegradable surfactant
without limiting the branching to methyl branches,
without limiting the branching to under 1.4, and without
limiting oneself to a ZSM 23 surface deactivated cata-
lyst. It would also be desirable to make a biodegradable

surfactant without conducting oligomerization reactions
through zeolite catalysts, which are expensive and may
coke up or be used up quickly if one needs to build chain
length through the catalyst.

5   Another product, EXXAL 13, is derived from propylene
oligomerization through acid catalysis to a wide range of
mono-olefins, the range having an average of 13 carbon
atoms being distilled out, but containing some olefins in
the C_{10-15} range. The olefin is then subjected to

10   hydroformylation using an oxo process. EXXAL 13 is
reported to be a 3-4 methyl branched tridecyl-alcohol
known for its use in lubricants and in those detergent
formulations which do not require rapid biodegradation.
This is because EXXAL 13 only slowly biodegrades. While

15   such a high amount of branching is not necessary, it
would be desirable to make a surfactant having a higher
amount of branching for detergency which is nevertheless
readily biodegradable.

        US Patent 5,196,625 describes a dimerization process

20   for producing linear and/or mono -branched C_{10} to C_{28}
olefins using dimerization catalysts, for the production
of biodegradable alkylbenzene sulfonates detergents by
alkylating the olefins onto benzene.   No mention is made
of using the dimerized olefins to make alcohols.

25   Further, the patentee reported that it is generally
recognized that "linear and mono-branched alkyl aromatic
sulfonates are generally much more readily biodegraded
than multibranched alkyl aromatic sulfonates and, hence,
much more desirable as detergents." For this reason, the

30   patentee sought to ensure that the olefins made were
substantially linear and monobranched. Again, it would
be desirable to make highly branched products that have
good detergency and biodegradability from alcohols, and

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also without regard to limitations on the amount of
branching being low.

The patentee of US 4,670,606 likewise recommended
using "linear detergent oxo-alcohols or those in which
5   the linear fraction is as high as possible" for bio-
degradability reasons in the detergent field, while oxo-
alcohols that are highly branched are desirable as lubri-
cating oil additives because the branching depresses the
freezing point of the lubrication oil. Thus, the
10   invention was directed towards methods to separate the
two from a mixture.

The desire to make highly linear high olefin alcohols
was also expressed in US 5,488,174. In discussing the
problems encountered by cobalt carbonyl catalyzed hydro-
15   formylation of olefins, the patentee noted that this
process produced a composition which contained branched
compounds when starting with internal olefins, which was
particularly undesirable because of its poor biode-
gradability. Thus, the patentee recommended using
20   catalytic processes which would produce mixtures
exhibiting high linear/branching ratios.

As previously noted, the highly linear NEODOL alcohol
line of intermediates for the production of detergent
surfactants are commercially successful, in part because
25   of their high linearity rendering them readily
biodegradable. However, the high degree of linearity
also increased the hydrophobicity of the hydrophobe part
of the chain, thereby decreasing its cold water
solubility/detergency.   In general, the highly linear
30   alcohol sulfates suffer from poor cold water
solubility/detergency. Along with the concern for using
biodegradable compounds, government regulations are also
calling for the lowering of wash temperatures.

Thus, there exists a growing need for alcohol
intermediates which are both biodegradable and exhibit
good detergency at cold wash temperatures. The solution
to this problem was not merely as simple as increasing

5   the branching of the higher olefin alcohol in order to
decrease hydrophobicity and thereby hopefully increase
cold water detergency, because as noted above it is well
recognized that branched compounds exhibit poor bio-
degradability.

10   3. Summary of the invention

There have now been found new compositions of
branched primary alcohols and their alkoxylate, sulfate
and alkoxy sulfate derivatives, which satisfy require-
ments for biodegradability and cold water detergency, and

15   processes for the production of these compositions.

The present invention therefore firstly relates to a
branched primary alcohol composition, having from 8 to
36 carbon atoms and an average number of branches per
molecule of from 0.7 to 3.0, said branching comprising

20   methyl and ethyl branches.

The invention relates secondly to a process for
preparing said branched primary alcohol composition,
which process comprises the steps of:

a)   contacting an olefin feed comprising a linear olefins

25   having at least 7 carbon atoms with a catalyst effective
for skeletally isomerising said linear olefin to yield a
branched olefin of the same carbon number; and

b)   converting said branched olefin to said primary
alcohol composition.

30   The term "skeletal isomerisation", as used herein,
refers to hydrocarbon isomerisation wherein straight
chains are converted, at least in part, to branched
chains of the same number of carbon atoms. The catalyst

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of step a) is preferably a zeolite having at least one channel with a crystallographic free diameter ranging from 0.42 to 0.70 nanometer. The conversion to alcohol in step b) is preferably by hydroformylation.

5   The invention relates thirdly to a different process for preparing said branched primary alcohol composition, having from 13 to 21 carbon atoms, which process comprises the steps of:

a)   dimerising, in the presence of a homogeneous dimeri-

10   sation catalyst, an olefin feed comprising a C_6-C_{10} olefin to yield a C_{12}-C_{20} branched olefin; and

b)   Converting said C_{12}-C_{20} branched olefin to said branched primary alcohol composition.

The olefin feed of step a) is preferably linear

15   olefin and preferably comprises at least 85 wt% of C_6-C_{10} olefins. Step a) is preferably a one-step dimerisation process. The homogenous catalyst preferably comprises a mixture of a nickel carboxylate or a nickel chelate, with an alkyl aluminium halide or an alkyl aluminium alkoxide.

20   Optionally the branched olefin produced in step a) is subjected to a double-bond isomerisation step before embarking on step b). The conversion to alcohol in step b) is preferably by hydroformylation.

The invention relates in the fourth place to a

25   branched primary alcohol alkoxylate composition, pre-parable by reacting said branched primary alcohol composition with an oxirane compound.

The invention relates in the fifth place to a branched primary alkyl sulphate, preparable by sulfating

30   said branched a primary alcohol composition.

And in the sixth place the invention relates to a deter-gent composition comprising:

a)   one or more surfactant(s) selected from the group of
said branched primary alcohol alkoxylates, branched
primary alkyl sulphates, and branched alkoxylated primary
alkyl sulphates;

b)   a builder; and

c)   optionally one or more additives selected from the
group of foam controlling agents, enzymes, bleaching
agents, bleach activators, optical brighteners, co-
builders, hydrotropes and stabilisers.

4.   Detailed Description of the Invention.

As used herein, the phrase average number of branches
per molecule chain refers to the average number of
branches per alcohol molecule, as measured by ^{13}C Nuclear
Magnetic Resonance (^{13}C NMR) as discussed below. The
average number of carbon atoms in the chain are
determined by gas chromatography.

Various references will be made throughout this
specification and the claims to the percentage of
branching at a given carbon position, the percentage of
branching based on types of branches, average number of
branches, and percentage of quaternary atoms. These
amounts are to be measured and determined by using a
combination of the following three ^{13}C-NMR techniques.
(1) The first is the standard inverse gated technique
using a 45-degree tip ^{13}C pulse and 10 s recycle delay
(an organic free radical relaxation agent is added to the
solution of the branched alcohol in deuterated chloroform
to ensure quantitative results). (2) The second is a
J-Modulated Spin Echo NMR technique (JMSE) using a
1/J delay of 8 ms (J is the 125 Hz coupling constant
between carbon and proton for these aliphatic alcohols).
This sequence distinguishes carbons with an odd number of

protons from those bearing an even number of protons, i.e. CH_3/CH vs CH_2/C_q (C_q refers to a quaternary carbon). (3) The third is the JMSE NMR "quat-only" technique using a 1/2J delay of 4 ms which yields a spectrum that contains signals from quaternary carbons only. The JSME NMR quat only technique for detecting quaternary carbon atoms is sensitive enough to detect the presence of as little at 0.3 atom% of quaternary carbon atoms. As an optional futher step, if one desires to confirm a conclusion reached from the results of a quat only JSME NMR spectrum, one may also runa DEPT-135 NMR sequence. We have found that the DEPT-135 NMR sequence is very helpful in differentiating true quaternary carbons from breakthrough protonated carbons. This is due to the fact that the DEPT-135 sequence produces the "opposite" spectrum to that of the JMSE "quat-only" experiment. Whereas the latter nulls all signals except for quaternary carbons, the DEPT-135 nulls exclusively quaternary carbons. The combination of the two spectra is therefore very useful in spotting non quaternary carbons in the JMSE "quat-only" spectrum. When referring to the presence or absence of quaternary carbon atoms throughout this specification, however, we mean that the given amount or absence of the quaternary carbon is as measured by the quat only JSME NMR method. If one optionally desires to confirm the results, then also using the DEPT-135 technique to confirm the presence and amount of a quaternary carbon.

The detergency evaluations conducted and as used throughout were based from a standard high density laundry powder (HDLP) Detergency/Soil Redeposition Performance test. The evaluations in the working examples were conducted using Shell Chemical Company's

radiotracer techniques at the designated temperatures in
Table III at a water hardness of 150 ppm as CaCO$_3$
(CaCl$_2$/MgCl$_2$ = 3/2 on a molar basis). The primary alcohol
sulfated compositions of the invention were tested, on a
1/4 cup basis, against multisebum, cetanesqualane and
clay soiled permanent press 65/35 polyester/cotton
(PPPE/C) fabric. The HDLP's were tested at 0.74 g/l
concentration, containing 27 wt% of the primary alcohol
sulfate composition, 46 wt% of builder (zeolite-4A), and
27 wt% of sodium carbonate.

The composition of the radiolabeled Multisebum Soil
was as follows:

Component	Label	%wt.
Cetane	3H	12.5
Squalane	3H	12.5
Trisearin	3H	10
Arachis (Peanut) Oil	3H	20
Cholesterol	14C	7
Octadecanol	14C	8.0
Oleic Acid	14C	15.0
Stearic Acid	14C	15.0

A Terg-O-Tometer was used to wash the swatches at
15 minute intervals. The wash conditions were set to
measure both cold water detergency at 10 °C and warm
water detergency at 36 °C. The agitation speed was
100 rpm. Once the 4" x 4" radiotracer soiled swatches
were washed by the Terg-O-Tometer, they were hand
rinsed. The wash and rinse waters were combined for
counting to measure sebum soil removal. The swatches were
counted to measure clay removal.

For details concerning the detergency methods and
radiotracer techniques, reference may be had to
B.E. Gordon, H. Roddewig and W.T Shebs, HAOCS, 44:289
(1967), W.T. Shebs and B.E. Gordon, JAOCS, 45:377 (1968),
and W.T. Shebs, Radioisotope Techniques in Detergency,
Chapter 3, Marcel Dekker, New York (1987.

The biodegradation testing methods for measuring the
biodegradability of the working example sulfates were
conducted in accordance with the test methods established
in 40 CFR §796.3200, also known as the OECD 301D test
method. By a biodegradable primary alcohol sulfate compo-
sition or surfactant is meant that that the compound or
composition gives a measured biochemical oxygen demand
(BOD) of 60% or more within 28 days, and this level must
be reached within 10 days of biodegradation exceeding
10 percent.

The primary alcohol composition of the invention
contains an average chain length per molecule ranging
from 8-36 carbon atoms. For many surfactant appli-
cations, such as detergents, the alcohol composition
contains an average carbon chain length of 11, 12, 13,
14, 15, 16, 17, 18, 19, 20 or 21 carbon atoms, or any
decimal inbetween, expressed as an average within the
range of 11 to 21 carbon atoms. The number of carbon
atoms includes carbon atoms along the chain backbone as
well as branching carbons.

Preferably, at least 75 wt%, more preferably, at
least 90 wt.% of the molecules in the primary alcohol
composition have chain lengths ranging from 11 to 21, yet
more preferably from 14 to 18 carbon atoms. As one
feature of the invention, the average number of branches
is at least 0.7, as defined and determined above. The
compositions having an average number of branches of at

least 1.5, in particular ranging from 1.5 to about 2.3, especially from 1.7 to 2.1, achieve a good balance of cold water detergency and biodegradability when sulfated. Conventional linear alcohol sulfates contain an average number of branches of only 0.05 to 0.4, and are quite biodegradable. Up to this point, however, the introduction of a higher degree of branching for the purpose of improving cold water detergency has lead to failures in biodegradability tests. The primary alcohol composition of the invention, when sulfated, has the advantage of introducing a large number of branches to improve its cold water properties without sacrificing biodegradability. The cold water properties are improved when the amount of branching is at least 1.5.

A feature of the invention lies in the provision of a primary alcohol composition as defined above, having less than 0.5 atom% of C_q's as measured by a quat only JMSE modified ^{13}C-NMR having a detection limit of 0.3 atom% or better, and preferably an primary alcohol composition which contains no C_q's as measured by this NMR technique. For reasons not yet clearly understood, it is believed that the presence of C_q's on an alcohol molecule prevents the biodegradation of that particular sulfated molecule by biological organisms. Alcohols containing as little as 1 atom% of C_q's have been been found to biodegrade at failure rates. It is also believed that previous attempts at the introduction of a high degree of branching has led to the formation of a sufficient number of C_q's to account for biodegradation failure.

In a preferred embodiment of the invention, less than 5%, or more preferably less than 3%, of the alcohol molecules in the primary alcohol composition are linear

alcohols. The efficient reduction in the number of linear alcohols to such a small amount in the composition results from introducing branching on an olefin feedstock by a skeletal isomerization or dimerisation technique using efficient catalysts as described further below, rather than introducing branching by methods such as acid catalyzed oligomerization of propylene molecules, or zeolite catalyzed oligomerization techniques. In a more preferable embodiment, the primary alcohol composition contains less than 3% of linear alcohols. The percentage of molecules which are linear may be determined by gas chromatography.

When the branching has been achieved by skeletal isomerization, the primary alcohol composition of the invention may be characterized by the NMR technique as having from 5 to 25% branching on the C_2 carbon position, relative to the hydroxyl carbon atom. In a more preferred embodiment, from 10 to 20% of the number of branches are at the C_2 position, as determined by the NMR technique. The primary alcohol composition also generally has from 10% to 50% of the number of branches on the C_3 position, more typically from 15% to 30% on the C_3 position, also as determined by the NMR technique. When coupled with the number of branches seen at the C_2 position, the primary alcohol composition in this case contain significant amount of branching at the C_2 and C_3 carbon positions.

Not only do the primary alcohol composition of the invention have a significant number of branches at the C_2 and C_3 positions, but we have also seen by the NMR technique that many of the primary alcohol compositions have at least 5% of isopropyl terminal type of branching,

meaning methyl branches at the second to last carbon
position in the backbone relative to the hydroxyl carbon.
We have even seen at least 10% of terminal isopropyl
types of branches in the primary alcohol composition,
typically in the range of 10% to 20%. In typical hydro-
formylated olefins of the NEODOL series, less than 1%,
and usually 0.0%, of the branches are terminal isopropyl
branches. By skeletally isomerizing the olefin according
to the invention, however, the primary alcohol compo-
sition contains a high percentage of terminal isopropyl
branches relative to the total number of branches.

Considering the combined number of branches occurring
at the C_2, C_3, and isopropyl positions, there are embodi-
ments of the invention where at least 20%, more pre-
ferably at least 30%, of the branches are concentrated at
these positions. The scope of the invention, however,
includes branching occurring across the length of the
carbon backbone. In another preferred embodiment of the
invention, the total number of methyl branches number at
least 40%, even at least 50%, of the total number of
branches, as measured by the NMR technique described
above. This percentage includes the overall number of
methyl branches seen by the NMR technique described above
within the C_1 to the C_3 carbon positions relative to the
hydroxyl group, and the terminal isopropyl type of methyl
branches.

Significantly, we have consistently observed a signi-
ficant increase in the number of ethyl branches over
those seen on NEODOL alcohols. The number of ethyl
branches can range from 5% to 30%, most typically from
10% to 20%, based on the overall types of branching that
the NMR method detects. Thus, the skeletal isomerization
of the olefins produced both methyl and ethyl branches,

and these alcohols, when sulfated, alkoxylated, or both, worked exceedingly well in biodegradability and detergency tests. Thus, the types of catalysts one may use to perform skeletal isomerization are not restricted to

5 those which will produce only methyl branches. The presence of a variety of branching types is believed to enhance a good overall balance of properties.

The olefins used in the olefin feed for skeletal isomerization are at least C_7 mono-olefins. In a

10 preferred range, the olefin feed comprises C_7 to C_{35} mono-olefins. Olefins in the C_{11} to C_{19} range are considered most preferred for use in the instant invention, to produce primary alcohol compositions in the C_{12} to C_{20} range, which are the most common ranges for deter-

15 gent applications. As a general rule, the higher the carbon number of the surfactant derivative, the more noticeable are the improvements in physical properties and formulateability.

In general, the olefins in the olefin feed composi-

20 tion are predominately linear. Attempting to process a predominately branched olefin feed, containing quaternary carbon atoms or extremely high branch lengths, would require separation methods after passing the olefin stream across the catalyst bed to separate these species

25 from the desired branched olefins. While the olefin feed can contain some branched olefins, the olefin feed processed for skeletal isomerization preferably contains greater than about 50 percent, more preferably greater than about 70 percent, and most preferably greater than

30 about 80 mole percent or more of linear olefin molecules.

The olefin feed generally feed does not consist of 100% olefins within the specified carbon number range, as

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such purity is not commercially available. The olefin
feed is usually a distribution of mono-olefins having
different carbon lengths, with at least 50 wt.% of the
olefins being within the stated carbon chain range or
digit, however specified. Preferably, the olefin feed
will contain greater than 70 wt.%, more preferably about
80 wt.% or more of mono-olefins in a specified carbon
number range (e.g., C_7 to C_9, C_{10} to C_{12}, C_{11} to C_{15}, C_{12}
to C_{13}, C_{15} to C_{18}, etc.), the remainder of the product
being olefin of other carbon number or carbon structure,
diolefins, paraffins, aromatics, and other impurities
resulting from the synthesis process.The location of the
double bond is not limited. The olefin feed composition
may comprise α-olefins, internal olefins, or a mixture
thereof.

Chevron Alpha Olefin product series (trademark of and
sold by Chevron Chemical Co.), manufactures predominantly
linear olefins by the cracking of paraffin wax. Commer-
cial olefin products manufactured by ethylene oligomeri-
zation are marketed in the United States by Shell Chemi-
cal Company under the trademark NEODENE and by Ethyl
Corporation as Ethyl Alpha-Olefins. Specific procedures
for preparing suitable linear olefins from ethylene are
described in U.S. Patent Nos. 3,676,523, 3,686,351,
3,737,475, 3,825,615 and 4,020,121. While most of such
olefin products are comprised largely of alpha-olefins,
higher linear internal olefins are also commercially
produced, for example, by the chlorination-dehydro-
chlorination of paraffins, by paraffin dehydrogenation,
and by isomerization of alpha-olefins. Linear internal
olefin products in the C_8 to C_{22} range are marketed by
Shell Chemical Company and by Liquichemica Company.

The catalyst used for skeletal isomerization pre-
ferably contains a zeolite having at least one channel
with a crystallographic free channel diameter ranging
from 0.42 to 0.70 nanometer, measured at room tempera-
5   ture, with essentially no channel present which has a
free channel diameter which is greater than
0.70 nanometer.

The skeletal isomerization catalyst should contain at
least one channel having a crystallographic free diameter
10   at the entrance of the channel within the stated range.
The catalyst should not have a diameter at the entrance
of a channel which exceeds the 0.70 nanometer upper limit
to the range. Zeolites possessing channel diamters
greater than 0.7 nm are susceptible to unwanted aromati-
15   zation, oligomerization, alkylation, coking and by-
product formation. On the other hand, if the zeolite does
not contain a channel having a free diameter along either
of the x or y planes of at least 0.42 nm, the channel
size becomes too small to allow diffusion of the olefin
20   into and out of the channel pore once the olefin becomes
branched. Thus, the zeolite must have at least one
channel with free diameters of that channel within the
range of 0.42 to 70 nm. All other specifications are
preferences.

25   Without being bound to a theory, it is believed that
the olefin molecule, due to its high carbon chain length,
does not have to enter into the zeolite channel, diffuse
through, and exit the other end of the channel. The rate
of branching seen when passing the olefin feed across the
30   zeolite does not correspond to the theoretical rate of
branching if each olefin molecule were to pass through
the channels. Rather, it is believed that most of the
olefins partially penetrate the channel for a distance

effective to branch the portion of the chain within the channel, and subsequently withdraw from the channel once isomerized. In this case, the olefin molecules in the composition would predominately have a structure which is

5   branched at the ends of the olefin carbon backbone, and substantially linear towards the center of the molecule, i.e., at least 25% of the carbons at the center are unbranched. The scope of the invention, however, includes branching anywhere along the carbon backbone

10   within the parameters described above with respect to the molecular structure.

Preferred embodiments of the zeolite structure are described in U.S. Patent No. 5,510,306. Zeolite struc- tures are also described in the Atlas of Zeolite Struc-

15   ture Types, by W.M. Meier and D.H. Olson. With respect to structure, in a preferred embodiment, the catalyst contains a channel having free diameters within the range of greater than 0.42 nm to less than 0.70 nm long both the x and y planes in the [001] view. Zeolites with this

20   specified channel size are typically referred to as medium or intermediate channel zeolites and typically have a 10-T member (or puckered 12-T member) ring channel structure in one view and a 9-T member or less (small pore) in another view, if any. There is no limit to the

25   number of channels or their orientation (parallel, non- interconnecting intersections, or interconnecting at any angle) in the zeolite. There is also no limit to the size of the channels which are outside of the stated range in both the x and y planes, so long as these other

30   channels do not have free diameter in either of the x or y planes which is greater than 0.70 nm. For example, other channels having a free diameter of 0.42 nm or less

in one or both of the x or y are within the scope of the invention.

There is also no limit on the number of dimensions, one, two, or three, that the channel system may have. While the scope of the invention includes two or three dimensional zeolites with interconnecting channels having any size less than 0.70 nm, and including at least one channel within the stated range, there may exist limited circumstances where, for example, α-olefins may meet at the intersection of the interconnecting channels and dimerize or oligomerize, depending on the size of the olefin, the proximity of the interconnecting intersection to the channel entrances, the size of the interconnecting intersection, temperature, flow rates, among other factors. While it is unlikely that such dimer could diffuse back out of the zeolite, the dimer may coke the catalyst or crack within the channel structure, forming by-product olefins having quaternary carbon branching. Thus, the interconnecting channel system in a two or three dimensional zeolite should have free diameters effective to prevent the formation of dimers, trimers, or oligomers under the given processing conditions, which when cracked, can produce quaternary branched by-products. In a preferred embodiment, all channels interconnecting to the channel within the stated range have free diameters in both of the x and y planes of 0.42 nm or less in order to eliminate the possibility that two olefin molecules would contact each other within the zeolite and dimerize or trimerize. This preference, however, applies only to interconnecting channels. A zeolite containing more than one channel, whether one, two, or three dimensional or even intersecting on different planes, but none of which interconnect, does

not raise the possibility of dimerization or trimeriza-
tion because the channels do not connect. Thus, there is
no preference for these types of structures, so long as
the basic requirements noted above are observed.

5   Examples of zeolites, including molecular sieves,
that can be used in the processes of this invention with
a channel size between 0.42 and 0.70 nm, include ferrie-
rite, AlPO-31, SAPO-11, SAPO-31, SAPO-41, FU-9, NU-10,
NU-23, ZSM-12, ZSM-22, ZSM-23, ZSM-35, ZSM-48, ZSM-50,
10   ZSM-57, SUZ-4A, MeAPO-11, MeAPO-31, MeAPO-41, MeAPSO-11,
MeAPSO-31, and MeAPSO-41, MeAPSO-46, ELAPO-11, ELAPO-31,
ELAPO-41, ELAPSO-11, ELAPSO-31, and ELAPSO-41, laumon-
tite, cancrinite, offretite, hydrogen form of stilbite,
the magnesium or calcium form of mordenite and partheite.
15   The isotypic structures of these frameworks, known under
other names, are considered to be equivalent. An overview
describing the framework compositions of many of these
zeolites is provided in New Developments in Zeolite
Science Technology, "Aluminophosphate Molecular Sieves
20   and the Periodic Table," Flanigen et al. (Kodansha Ltd.,
Tokyo, Japan 1986).

Many natural zeolites such as ferrierite, heulandite
and stilbite feature a one-dimensional pore structure
with a pore size at or slightly smaller than about
25   0.42 nm diameter. These same zeolites can be converted to
zeolites with the desired larger channel sizes by re-
moving the associated alkali metal or alkaline earth
metal by methods known in the art, such as ammonium ion
exchange, optionally followed by calcination, to yield
30   the zeolite in substantially its hydrogen form. See e.g.,
U.S. Pat. Nos. 4,795,623 and 4,942,027. Replacing the
associated alkali or alkaline earth metal with the
hydrogen form correspondingly enlarges the channel

diameter. It is understood that the channel diameter or "size" shall mean the effective channel diameter or size for diffusion. Alternatively, natural zeolites with too large a channel size, such as some forms of mordenite, can be altered by substituting the alkali metal with larger ions, such as larger alkaline earth metals to reduce the channel size and thus become useful for the processes of this invention.

Particularly preferred zeolites are those having the ferrierite isotypic framework structure (or homeotypic). See the Atlas of Zeolite Structure Types, by W. M. Meier and D. H. Olson, published by Butterworth-Heinemann, third revised edition, 1992, page 98. The prominent structural features of ferrierite found by x-ray crystallography are parallel channels in the alumino-silicate framework which are roughly elliptical in cross-section. Examples of such zeolites having the ferrierite isotypic framework structure include natural and synthetic ferrierite (can be orthorhombic or monoclinic), Sr-D, FU-9 (EP B-55,529), ISI-6 (U.S. Pat. No. 4,578,259), NU-23 (E.P. A-103,981), ZSM-35 (U.S. Pat. No. 4,016,245) and ZSM-38 (U.S. Pat. No. 4,375,573). The hydrogen form of ferrierite (H-ferrierite) is the most preferred zeolite and considered to be substantially one-dimensional, having parallel running channels, with elliptical channels having free diameters of 0.42 x 0.54 nm along the x and y planes in the [001] view, which is large enough to permit entry of a linear olefin and diffusion out of or through the channel of the methyl branched isoolefin and small enough to retard coke formation. Methods for preparing various H-ferrierite are described in U.S. Pat. Nos. 4,251,499, 4,795,623 and 4,942,027.

The skeletal isomerization catalyst used in the
isomerization processes of this invention may be combined
with a refractory oxide that serves as a binder material.
Suitable refractory oxides include natural clays, such as
5   bentonite, montmorillonite, attapulgite, and kaolin;
alumina; silica; silica-alumina; hydrated alumina;
titania; zirconia and mixtures thereof. The weight ratio
of zeolite to binder material suitably ranges from about
10:90 to about 99.5:0.5, preferably from about 75:25 to
10   about 99:1, more preferably from about 80:20 to about
98:2 and most preferably from about 85:15 to about 95:5
(anhydrous basis).

     Preferably the binder is, for example, selected from
the silicas, the aluminas, the silica-aluminas and the
15   clays. More preferred binders are aluminas, such as
pseudoboehmite, gamma and bayerite aluminas. These
binders are readily available commercially and are used
to manufacture alumina-based catalysts. LaRoche
Chemicals, through its VERSAL family of aluminas and
20   Vista Chemical Company, through its CATAPAL aluminas,
provide suitable alumina powders which can be used as
binders in preparing the instant catalysts (VERSAL and
CATAPAL are trade marks). Preferred alumina binders to be
used in the preparation of the catalyst, particularly
25   when extrusion is utilized, are the high-dispersity
alumina powders. Such high-dispersity aluminas have a
dispersity of greater than 50% in a aqueous acid
dispersion having an acid content of 0.4 milligram
equivalents of acid (acetic) per gram of Al_2O_3. Such
30   high-dispersity aluminas are exemplified by Vista's
CATAPAL D alumina.

Preferably, the skeletal isomerization catalyst is also prepared with at least one acid selected from monocarboxylic acids and inorganic acids and at least one organic acid with at least two carboxylic acid groups ("polycarboxylic acid"). Preferred monocarboxylic acid includes monocarboxylic acid having substituted or unsubstituted hydrocarbyl group having 1 to 20 carbon atoms which can be aliphatic, cyclic or aromatic. Examples include acetic acid, formic acid, propionic acid, butyric acid, caproic acid, glycolic acid, lactic acid, hydroxylbutyric acid, hydroxycyclopentanoic acid, salicylic acid, mandelic acid, benzoic acid, and fatty acids. Preferred inorganic acid includes mineral acids such as nitric acid, phosphoric acid, sulfuric acid and hydrochloric acid.

The preferred polycarboxylic acid is an organic acid with two or more carboxylic acid groups attached through a carbon-carbon bond linkage to an hydrocarbyl segment. The linkage can be at any portion of the hydrocarbyl segment. The polycarboxylic acid preferably has an hydrocarbyl segment from 0 to 10 carbon atoms which can be aliphatic, cyclic or aromatic. The hydrocarbyl segment has 0 carbon atoms for oxalic acid with two carboxylic acid groups attached through the carbon-carbon bond. Examples of the polycarboxylic acids includes, for example, tartaric acid, citric acid, malic acid, oxalic acid, adipic acid, malonic acid, galactaric acid, 1,2-cyclopentane dicarboxylic acid, maleic acid, fumaric acid, itaconic acid, phthalic acid, terephthalic acid, phenylmalonic acid, hydroxyphtalic acid, dihydroxyfumaric acid, tricarballylic acid, benzene-1,3,5-tricarboxylic acid, isocitric acid, mucic acid and glucaric acid. The polycarboxylic acids can be any isomers of the above

acids or any stereoisomers of the above acids. Poly-
carboxylic acids with at least two carboxylic acid groups
and at least one hydroxyl group is more preferred. The
most preferred second acids (i.e., polycarboxylic acids)
are citric acid, tartaric acid and malic acid.

Optionally, coke oxidation promoting metals can be
incorporated into the instant catalysts to promote the
oxidation of coke in the presence of oxygen at a
temperature greater than about 250 °C. While the term
"metal(s)" is used herein in reference to the oxidation
catalysts, these metals will not necessarily be in the
zero-valent oxidation state and in many cases will be in
the higher oxidation states. Thus, "metal(s)" can
encompass the oxides as well as the metals. Preferably
the coke oxidation-promoting metal(s) used are transition
and rare earth metals. More preferably the coke oxida-
tion-promoting metals are selected from Groups IB, VB,
VIB, VIIB and VIII of the transition metal series of the
Periodic Table. Specifically preferred are Pd, Pt, Ni,
Co, Mn, Ag and Cr. Most preferred are the Group VIII
metals palladium and/or platinum. The amount of metal
introduced can be up to about 2% by weight, measured as
the metal per total weight of the catalyst. When using
platinum and/or palladium, smaller rather than larger
amounts of metals incorporated into the zeolite/binder
are preferred. Preferably platinum and/or palladium will
range from 5 to 3000 ppm by weight, basis metal, of the
final catalyst.

In a preferred method, the instant catalysts can be
prepared by mixing a mixture of at least one zeolite as
herein defined, alumina-containing binder, water, at
least one monocarboxylic acid or inorganic acid and at
least one polycarboxylic acid in a vessel or a container,

forming a pellet of the mixed mixture and calcining the
pellets at elevated temperatures. In one preferred
embodiment zeolite powder and alumina-containing powder
is mixed with water and one or more of monocarboxylic
acid or inorganic acid (first acid) and one or more of
polycarboxylic acid (second acid) and optionally one or
more compounds of the coke-oxidation promoting metal and
the resulting mixture (paste) is formed into a pellet.
The coke-oxidation promoting metal may alternatively be
impregnated.

Preferably the pellet is formed by extrusion but can
also be formed into catalytically useful shape by
pressing hydrostatically or mechanically by pressing into
die or mold. When extrusion is used optional extrusion
aids such as cellulose derivatives, e.g., METHOCEL F4M
hydroxypropyl methylcellulose (METHOCEL is a trade mark),
can be utilized (manufactured by The Dow Chemical
Company). The term "pellets" as used herein can be in any
shape or form as long as the materials are consolidated.
The formed pellets are calcined at a temperature ranging
from a lower range of from 200 °C., preferably from
300 °C., more preferably from 450 °C, to an upper range
of up to 700 °C., preferably up to 600 °C., more
preferably up to 525 °C.

The ratio of the first acids to second acids is
preferably within the range of 1:60 to 60:1, more
preferably 1:10 to 10:1. The amount of the first acid
used is in an amount effective to peptize the mixture.
Preferably the amount of the first acid used is from 0.1
to 6 weight percent, more preferably from 0.5 to about
4 weight percent based on the combined weight of zeolite
and alumina-containing binder (anhydrous solids basis).

Aluminas with lower dispersibilities than Vista CATAPAL D
may require greater amounts of acid to peptize them. The
amount of the second acid used is in an amount effective
to promote the catalytic activity of the catalyst which
is from 0.1 to 6, preferably from 0.2 to 4 weight percent
based on the combined weight of zeolite and alumina-
containing binder (anhydrous solids basis).

The mixture is mixed thoroughly or vigorously until
the mixture appears uniform. The mixing can be performed
by combining all of the components of the mixture at once
or by adding the components of the mixture at different
stages of mixing. The mixing can be accomplished by
mulling. The term "mulling" is used herein to mean mixing
of powders to which sufficient water has been added to
form a thick paste and wherein the mixing is accompanied
by shearing of the paste. Commercially available mullers
such as the Lancaster Mix Muller and the Simpson Mix
Muller can be used to carry out the mixing. A commercial
blender such as a ribbon blender and/or a powder mill can
also be used to carry out the mixing.

Optionally the coke-oxidation promoting metal can be
impregnated to the formed pellet with a metals-containing
solution instead of mixing in the paste mixture.

The temperature at which the skeletal isomerization
may be conducted may range from 200 °C to 500 °C. Tem-
peratures should not exceed the temparture at which the
olefin will crack. Suitable pressures maintained during
the isomerization reaction is at an olefin partial
pressure ranging from 10 to 1000 kPa, more preferably
from above 50 to 500 kPa, most preferably above 50 to
200 kPa.

High conversion, high selectivity, and high yields
are attained by the process of the present invention.
The olefin feed comprising linear olefins having an
average of at least 7 carbon atoms are contacted with a

5   catalyst effective for skeletally isomerizing said linear
olefins at a conversion of at least 40% in a single pass.
However, the process of the invention enables one to
skeletally isomerize the linear olefins at far higher
conversions. Conversions of at least 70%, preferably at

10   least 80%, more preferably at least 90%, and most
preferably at least 95% are attainable in a single pass
in the process of the invention. Advantageously, the
conversion percentages are obtainable at temperatures
ranging from 200 °C to 500 °C, preferably at temperatures

15   ranging from 200 °C to 350 °C.

The catalyst employed in the skeletal isomerization
process is also highly selective towards the manufacture
of skeletally isomerized branched olefins. Although high
selectivities are attainable according to the skeletal

20   isomerization process, the selectivity of the catalyst
towards the manufacture of C7 or higher branched olefins
from a linear C7 or higher linear olefin stream is at
least 30% in one pass since processes using catalysts
with lower selectivities are not regarded as sufficiently

25   effective or economically justified. Higher
selectivities of at least 70%, more preferably at least
80%, most preferably at least 90%, and even as high as at
least 95%, are attainable in the process of the invention
in one pass.

30   Another advantage observed by skeletally isomerizing
the C7 or higher linear olefin streams according to the
process of the invention is that high conversion of the
linear olefin stream can be obtained in conjunction with

high selectivity to the skeletally isomerized branched olefins. The olefin stream is preferably converted at percentages of at least 70%, with a selectivity to the skeletally isomerized branched olefins of at least 70%, more preferably at least 80%, most preferably at least 90%. In another embodiment, at least 80% of the olefin stream is converted, at a selectivity to the skeletally isomerized branched olefins of at least 80%, more preferably a selectivity of at least 90%, most preferably at least 95% selectivity. In a further embodiment, at least 90% of the olefins are converted at selectivities of 90% or more toward the skeletally isomerized branched olefins, more preferably at selectivities of 95% or more.

The skeletal isomerization process also produces high yields of skeletally isomerized branched olefins. The yield of the skeletally isomerized branched olefins should be at least about 10%, but yields of at least about 50%, more preferably at least about 65%, most preferably at least about 80%, and even as high as at least about 90% are achievable in practice. The highest yield of skeletally isomerized branched olefin obtained is limited by the equilibrium concentration of the branched olefins at the skeletal isomerization temperature.

The present skeletal isomerization process can be operated at a wide range of conditions. Olefin weight hour space velocity of the olefin can range from 0.1 to 100 per hour. Preferably, the WHSV is between 0.5 to 50, more preferably between 1 and 40, most preferably between 2 and 30 per hour. At lower WHSV's, it is possible to operate at lower temperatures while achieving high yields of skeletally isomerized branched olefins. At higher WHSV's, the temperature is generally increased in order

to maintain the desired conversion and selectivity to the skeletally isomerized branched olefins. Further, optimal selectivities are generally achieved at lower olefin partial pressures mentioned above. For this reason, it is

5   often advantageous to dilute the feed stream with a diluent gas such as nitrogen or hydrogen. Although reducing the olefin partial pressure with a diluent may be beneficial to improve the selectivity of the process, it is not necessary to dilute the olefin stream with a

10 diluent.

      If a diluent is used, the molar ratio of olefin to diluent can range from 0.01:1 to 100:1, and is generally within the range of 0.1:1 to 5:1.

      When the branching has been achieved by dimerisation,

15 the primary alcohol composition of the invention have relatively few branch points at the C_1 through C_3 carbon positions relative to the hydroxyl carbon and little or no isopropyl terminations, that is, little or no branches at the second to last carbon atom along the backbone of

20 the alcohol molecule relative to the hydroxyl carbon atom. In particular, the typical alcohol molecule in this case contains less than 25% branching at the C_2 and C_3 positions, and less than 5% isopropyl termination, more usually no isopropyl groups being detected.

25   From these carbon positions, the alcohol molecules made from the dimerised olefins look similar to the NEODOL alcohols. However, unlike the NEODOL alcohols which are predominately linear, the primary alcohol composition of the invention has a very high average

30 number of branches per molecule. Due to large number of branches found in the primary alcohol composition of the invention and the relatively low percentage of branch

points at the C_2, C_3, and isopropyl terminal carbon positions, the majority of the branches are toward the center of the molecule, with a significant number of the branches being located on one or both of the dimerized carbon atoms. The NMR spectral data is consistent with where the branches are thought to be located based on a chemical reaction equation.

The types of branching found in the primary alcohol composition of the invention varies from methyl, ethyl, propyl, and butyl or higher. A significant number of the branches detected by the NMR were ethyl groups, although this can vary depending upon the composition of the feed and reaction conditions. In one embodiment, however, the number of ethyl groups in the primary alcohol composition of the invention range, preferably, from 10 % to 30%, which is a significant jump from the amount of ethyl groups detected in NEODOL alcohols. The number of methyl groups detected by the NMR can also vary widely for the same reason. Typically, however, the number of methyl groups will range from 10% to 50%, as detected by the NMR.

Broadly speaking, a primary alcohol composition is obtained by dimerizing an olefin feed comprising C_6-C_{10} linear olefins in the presence of a dimerization catalyst under dimerization conditions to obtain C_{12}-C_{20} olefins.

In one embodiment, the olefin feed comprises at least 85 mol%, preferably at least 90 mol%, more preferably at least 95 mol% linear olefins. The remainder of the olefin feed comprises only a small number of branched olefins, preferably less than 3 mol%.

The olefin feed can contain shorter or longer olefins. In a preferred embodiment, however, the olefin

stream also comprises at least 85 wt% of the C_6-C_{10}

olefins, more preferably 90 wt%, and most preferably

95 wt% C_6-C_{10} olefins. Another advantage of the process

of the invention is that one can make mixtures of both

5   odd and even numbered dimerized olefins by employing

mixtures of both odd and even numbered olefins in the

feed, as distinguished from those processes which rely

upon oligomerizing either C_3 or C_4 olefins to build

higher olefins.

10   The olefin feed can be made up of internal or alpha

olefins, or mixtures thereof. Preferably, the majority

of the olefins present in the feed comprise internal

olefins because the dimerization of these olefins tend to

produce a variety of branch types, that is, methyl,

15   ethyl, and propyl branches, even butyl branches. By a

majority is meant that greater than 50 wt% of the olefin

feed is comprised of internal olefins. More preferably,

at least 75 wt% of the olefin feed is comprised of

internal olefins.

20   In one embodiment of the invention, there is provided

a one-step dimerization process.

By a one-step dimerization process is meant that an

olefin feed, once dimerized, is not further subjected to

dimerization. A one-step process does, however, include

25   recycling unreacted olefin feed to the dimerization zone

because this unreacted olefin was not dimerized. It also

includes a continuous process or several batch reactors

operating in parallel, so long as one dimerized stream of

olefin is not fed to a subsequent dimerization reaction

30   zone for a second or subsequent dimerization. This one

step process provides the advantage that one may use

conventional streams of olefins without the necessity for

expensive and sophisticated extraction and separation
processes for making an olefin stream of high purity
linear olefins. The olefin feed may be obtained by the
conventional oligomerization of ethylene, which may
subsequently be disproportionated, or by the Fischer-
Tropsch process, which uses a 1 carbon oligomerization by
passing CO and H_2 over iron or cobalt catalyst; as
distinguished from trimer or tetramer feeds of C_3 or C_4
olefins which are highly branched or require special
extraction steps to obtain high linearity in the olefin
feed.

Typically, the dimerization is conducted at tempera-
tures in the range of from about -10 °C to 100 °C.,
preferably from 20° to 50 °C for the duration of 1/2 to
8 hours, preferably 1 to 5 hours, using an olefin to
catalyst mole ratio of 200 to 20,000, preferably 1,000 to
10,000 moles of olefin per mole of catalyst. The dimeri-
zation is generally conducted as a liquid phase reaction
using pressures in the range of 0 to 300 kPa, preferably
100 to 200 kPa. Where the dimerization is conducted as a
batch process, the catalyst can be conveniently prepared
in situ in the reactor. The dimerization can also be con-
ducted as a continuous, semi-batch or multi-step process.
It should be appreciated that where typical or preferred
process conditions (e.g., temperatures, times, catalyst
ratios, etc.) have been given, that other process
conditions could also be used. Optimum reaction con-
ditions (e.g., temperature, reaction time, reactant
ratios, catalyst ratios, solvents, etc.) may vary with
the particular reactants, catalysts, or solvents used,
but can be determined by routine optimization procedures.

The dimerization catalysts of this invention can be
prepared by contacting the appropriate components of the
catalyst in the olefin to be dimerized. Preferably, the
components of the catalyst are not mixed together prior
5   to their addition to the olefin feed, as this may cause
decomposition of the catalyst. Added solvents, such as
chlorobenzene or cyclohexane may be used and do not
detract from catalyst performance.

The selection of the catalyst for the dimerization is
10   one which is selective towards the manufacture of high
yields of dimerized olefins having and average of from
0.7 to 3.0 and preferably 0.9 to 2.0 branches per
molecule. These catalysts are preferably soluble in
hydrocarbon media, for example, the olefin feed stream.
15   Examples of dimerization catalysts soluble in hydro-
carbons are complexes wherein a metal, preferably nickel,
is bound to at least one hydrocarbon group, for example a
bis- nickel, a nickel halide or bis-cyclooctadiene nickel
associated to a halogenated aluminium compound. Another
20   type of catalyst consists of the complexes formed by
admixing at least one nickel compound with at least one
alkylaluminium compound and optionally a ligand, for
example a phosphine. These catalysts are well-known in
the art. Illustrations of the catalyst that can be used
25   in this type of process are given in U.S. Patent
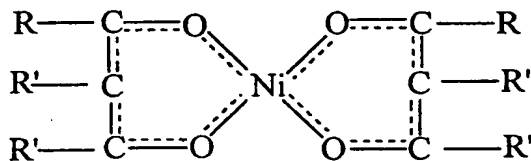Nos. 4,366,087; 4,326,650; and 4,398,049.

A preferred class of catalysts used in the process
are homogenous catalysts comprising a combination of a
nickel carboxylate or a nickel chelate, with an alkyl
30   aluminium halide or an alkyl aluminium alkoxide,
respectively. The Al/Ni mole ratio is suitably from 1.0
to 20.0.

The nickel compound comprises a nickel carboxylate or
a nickel chelate. The carboxylate of the nickel carbo-
xylate may be represented by the formula $(RCOO)_2Ni$, where
R is a branched or unbranched, hydrocarbyl radical, for
example an alkyl, cycloalkyl, alkenyl, aryl, aralkyl or
alkaryl radical, containing at least 2 carbon atoms,
preferably a sufficient number of carbon atoms to render
it compatible with hydrocarbon media, such as a hydro-
carbyl radical of 5-20 carbon atoms, which radical may be
substituted with, for example, hydroxy groups. One of the
RCOO- groups of the bivalent nickel carboxylate mentioned
above may optionally be substituted with group repre-
sented by R_1COO-, where R_1 is a halogenoalkyl radical
containing from 1 to 3 carbon atoms, as described in US
Patent No. 4,366,087.

Examples of the nickel carboxylates include, but are
not limited to, bis-(2-ethylhexanoate)nickel; 2-ethyl-
hexanoate nickel trichloro(or trifluoro) acetate;
2-ethylhexanoate nickel o-chlorobenzoate; and 2-ethyl-
hexanoate nickel acetylacetonate, nickel 2-ethylbutyrate
trifluoroacetate, nickel 2-ethylbutyrate trichloro-
acetate, nickel 3,3-dimethylbutyrate trifluoroacetate,
nickel 3,3-dimethylbutyrate trichloroacetate, nickel
4-methylvalerate trifluoroacetate, nickel heptanoate
trifluoroacetate, nickel heptanoate trichloroacetate,
nickel heptanoate tribromoacetate, nickel heptanoate
triiodoacetate, nickel 2-ethylhexanoate monofluoro-
acetate, nickel 2-ethylhexanoate trichloroacetate, nickel
2-ethylhexanoate dichloroacetate, nickel 2-ethylhexanoate
monochloroacetate, nickel 2-ethylhexanoate tribromo-
acetate, nickel 2-ethylhexanoate triiodoacetate, nickel
octoate trifluoroacetate, nickel octoate trichloro-
acetate, nickel decanoate trifluoroacetate, nickel

decanoate trichloroacetate, nickel myristate trifluoro-
acetate, nickel palmitate trifluoroacetate, nickel
dodecylbenzoate trifluoroacetate, nickel diisopropyl-
salicylate trichloroacetate, nickel myristate penta-
fluoropropionate and nickel 2-ethylhexanoate hepta-
fluorobutyrate.

The nickel chelate compounds, which react with the alkyl
aluminium alkoxides, are described in US Patent
Nos. 3,424,815 and 4,959,491. The nickel chelates include
those having the formula

$$R\text{---}C\text{===}O \quad O\text{===}C\text{---}R$$
$$R'\text{---}C \quad Ni \quad C\text{---}R'$$
$$R'\text{---}C\text{===}O \quad O\text{===}C\text{---}R' \qquad (I)$$

wherein R and R' independently are hydrogen, alkyl or
aryl of up to 10 carbon atoms, or haloalkyl or haloaryl
of up to 10 carbon atoms, with the proviso that the two
R' groups of each chelating ligand together with the
adjacent carbon atoms to which they are attached, can
form a six-membered carbocyclic aromatic ring of up to
4 halogen substituents. The halogenated chelating ligand
preferably has up to 15 carbon atoms and from 2 to
8 halogen substituents, but more preferably has up to
10 carbon atoms and from 3 to 6 halogen substituents. The
halogen substituents of the chelating ligand are suitably
fluorine, chlorine, bromine or iodine, wherein the R'
groups together form a divalent radical in which the
monoenol configuration is maintained as part of the
aromatic ring;

The aluminium compound comprises an hydrocarbyl
aluminium halide or a hydrocarbyl aluminium alkoxide.
The hydrocarbyl group generally comprises 0, 1 or
2 hydrocarbyl groups each having from 1 to 20 carbon

atoms, usually from 1 to 12 carbon atoms, the groups
including alkyl, aryl, aralkyl, alkaryl, and cycloalkyl.
The halide comprises 1 to 6 halides, such as fluoride,
iodide, chloride, or bromide, preferably whichever is
readily available, such as the chloride. Examples of the
hydrocarbyl aluminium halides include $AlCl_3$, ethyl-
aluminium dichloride, ethylaluminium sesquichloride,
dichloroethylaluminium, dichloroisobutylaluminium,
chlorodiethylaluminium or their mixtures.

Suitable alkoxides can be 1 or 2 alkoxide groups
whose alkyl segments are as defined above with respect to
the alkyl groups attached to the aluminium.

Optionally, the catalyst may also contain a small
amount of water which has the effect of increasing the
rate of the catalytic dimerization. Generally, the amount
of water employed will be an amount sufficient to
increase the rate of the catalytic dimerization.

At the outlet of the reactor, the catalyst may be
deactivated in known manner, for example, with ammonia
and/or an aqueous sodium hydroxide solution and/or an
aqueous sulfuric acid solution, or an organic acid/bi-
carbonate solution. The unconverted olefins and the
alkanes, if any, are separated thereafter from the
oligomers by distillation, or any other suitable
procedure, such as extraction, and the like. Unreacted
feedstock can be recycled back to the initial feedstock.

The branched - skeletally isomerized or dimerized -
olefins are subsequently converted to alcohols and to any
of a broad range of surfactants, including nonionic,
anionic, cationic, and amphoteric surfactants. The
branched olefin serves as a surfactant intermediate.
Specifically, the branched olefin serves as the hydro-
phobic moiety of the surfactant molecule, while the

moiety added to the olefin during the conversion process
serving as the hydrophile. Neither the particular
surfactant nor the means used to convert the branched
olefin to an alcohol or surfactant is considered critical
to the present invention, provided that it does not
rearrange the skeletal structure of the olefin to the
extent that the byproduct is no longer biodegradable, or
reduces the degree of branching to less than 0.7.

Conversion of the branched olefins to a primary
alcohol composition is conveniently accomplished, for
example, by hydroformylation, by oxidation and hydro-
lysis, by sulfation and hydration, by epoxidations and
hydration, or the like. In hydroformylation, the
skeletally isomerized olefins are converted to alkanols
by reaction with carbon monoxide and hydrogen according
to the Oxo process. Most commonly used is the "modified
Oxo process", using a phosphine, phosphite, arsine or
pyridine ligand modified cobalt or rhodium catalyst, as
described in U.S. Patent Nos. 3,231,621; 3,239, 566;
3,239,569; 3,239,570; 3,239,571; 3,420,898; 3,440,291;
3,448,158; 3,448,157; 3,496,203; and 3,496,204;
3,501,515; and 3,527,818. Methods of production are also
described in Kirk Othmer, "Encyclopedia of Chemical
Technology" 3rd Ed. vol 16, pages 637-653; "Monohydric
Alcohols: Manufacture, Applications and Chemistry",
E. J. Wickson, Ed. Am. Chem. Soc. 1981.

Hydroformylation is a term used in the art to denote
the reaction of an olefin with CO and H_2 to produce an
aldehyde/alcohol which has one more carbon atom than the
reactant olefin. Frequently, in the art, the term hydro-
formylation is utilized to cover the aldehyde and the
reduction to the alcohol step in total, i.e., hydro-
formylation refers to the production of alcohols from

olefins via carbonylation and an aldehyde reduction
process. As used herein, hydroformylation refers to the
ultimate production of alcohols.

Illustrative catalysts include cobalt hydrocarbonyl
catalyst, cobalt-phosphine ligand catalyst, and rhodium-
phosphine ligand catalyst. The choice of catalysts deter-
mines the various reaction conditions imposed. These
conditions can vary widely, depending upon the particular
catalysts. For example, temperatures can range from about
room temperatures to 300 °C. When cobalt carbonyl cata-
lysts are used, which are also the ones typically used,
temperatures will range from 150° to 250 °C. One of
ordinary skill in the art, by referring to the above-
cited references, or any of the well-known literature on
oxo alcohols can readily determine those conditions of
temperature and pressure that will be needed to hydro-
formylate the dimerized olefins.

Typical reaction conditions, however, are moderate.
Temperatures in the range of 125 °C to 200 °C are
recommended. Reaction pressures in the range of 2170 to
10440 kPa are typical, but lower or higher pressures may
be selected. Ratios of catalyst to olefin ranging from
1:1000 to 1:1 are suitable. The ratio of hydrogen to
carbon monoxide can vary widely, but is usually in the
range of 1 to 10, preferably about 2 moles of hydrogen to
one mole of carbon monoxide to favor the alcohol product.

The hydroformylation process can be carried out in
the presence of an inert solvent, although it is not
necessary. A variety of solvents can be applied such as
ketones, e.g. acetone, methyl ethyl ketone, methyl iso-
butyl ketone, acetophenone and cyclohexanone; aromatic
compounds such as benzene, toluene and the xylenes;

halogenated aromatic compounds such as chlorobenzene and orthodichlorobenzene; halogenated paraffinic hydrocarbons such as methylene chloride and carbon tetrachloride; paraffins such as hexane, heptane, methylcyclohexane and isooctane and nitriles such as benzonitrile and acetonitrile.

With respect to the catalyst ligand, mention may be made of tertiary organo phosphines, such as trialkyl phosphines, triamyl phosphine, trihexyl phosphine, dimethyl ethyl phosphine, diamylethyl phosphine, tricyclopentyl(or hexyl) phosphine, diphenyl butyl phosphine, dipenyl benzyl phosphine, triethoxy phosphine, butyl diethyoxy phosphine, triphenyl phosphine, dimethyl phenyl phosphine, methyl diphenyl phosphine, dimethyl propyl phosphine, the tritolyl phosphines and the corresponding arsines and stibines. Included as bidentate-type ligands are tetramethyl diphosphinoethane, tetramethyl diphosphinopropane, tetraethyl diphosphinoethane, tetrabutyl diphosphinoethane, dimethyl diethyl diphosphinoethane, tetraphenyl diphosphinoethane, tetraperfluorophenyl diphosphinoethane, tetraphenyl diphosphinopropane, tetraphenyl diphosphinobutane, dimethyl diphenyl diphosphinoethane, diethyl diphenyl diphosphinopropane and tetratrolyl diphosphinoethane.

Examples of other suitable ligands are the phosphabicyclohydrocarbons, such as 9-hydrocarbyl-9-phosphabicyclononane in which the smallest P-contianing ring contains at least 5 carbon atoms. Some examples include 9-aryl -9-phosphabicyclo[4.2.1]nonane, (di)alkyl-9-aryl -9-phosphabicyclo[4.2.1]nonane, 9-alkyl -9-phosphabicyclo[4.2.1]nonane, 9-cycloalkyl -9-phosphabicyclo-[4.2.1]nonane, 9-cycloalkenyl -9-phosphabicyclo-

[4.2.1]nonane, and their [3.3.1] and [3.2.1] counter-
parts, as well as their triene counterparts.

The branched primary alcohol composition of the
invention is suitable for the manufacture of anionic,
nonionic, and cationic surfactants, preferably the former
two, more preferably the anionic. Specifically, the
branched primary alcohol composition of the invention can
be used as the pecursor for the manufacture of anionic
sulfates, including alcohol sulfates and oxylakylated
alcohol sulfates, and nonionic oxyalkylated alcohols.

Any technique known for sulfating alcohols can be
used herein. The primary alcohol composition may be
directly sulfated, or first oxyalkylated followed by
sulfatation. A preferred class of compositions comprises
at least one anionic surfactant comprising the con-
densation product of the C_8 to C_{36}, particularly the C_{11}
to C_{19} branched primary alcohol composition with or
without ethylene oxide and/or propylene oxide, in which
the number of ethoxy groups ranges from 3 to 12 and the
ratio ethoxy/propoxy is from 4 to 12, followed by
sulfation.

The general class of anionic surfactants or alcohol
ethoxysulfates can be characterized by the chemical
formula:

$$R'-O-(CH_2-CH_2-O) \text{ x } -SO_3M(II)$$
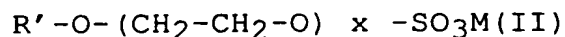
wherein R' represents the branched olefin hydrophobe
moiety, x represents the average number of oxyethylene
groups per molecule and is in the range of from 0 to 12,
and M is a cation selected from an alkali metal ion, an
ammonium ion, and mixtures thereof. Of course, the
surfactant can by oxyalkylated with any oxirane con-

taining compound other than, in mixture with, or
sequentially with ethylene oxide.

    Sulfonation processes are described, for instance, in
U.S. Patent Nos. 3,462,525, issued Aug. 19, 1969 to

5   Levinsky et. al., 3,428,654 issued Feb. 18, 1969 to
Rubinfeld et. al., 3,420,875 issued Jan. 7, 1969 to
DiSalvo et. al., 3,506,580 issued Apr. 14, 1970 to
Rubinfeld et. al., 3,579,537 issued May 18, 1971 to
Rubinfeld et. al., and 3,524,864 issued Aug. 18, 1970 to

10 Rubinfeld. Suitable sulfation procedures include sulphur
trioxide (SO_3) sulfation, chlorosulfonic acid ($ClSO_3H$)
sulfation and sulfamic acid (NH_2SO_3H) sulfation. When
concentrated sulfuric acid is used to sulfate alcohols,
the concentrated sulfuric acid is typically from 75 to

15 100, preferably from 85 to 98 percent by weight, in
water. Suitable amounts of sulfuric acid are generally in
the range of from 0.3 to 1.3, preferably from 0.4 to
1.0 mole of sulfuric acid per mole of alcohol.

    A typical sulphur trioxide sulfation procedure
20 includes contacting liquid alcohol or its ethoxylate and
gaseous sulphur trioxide at about atmospheric pressure in
the reaction zone of a falling film sulfator cooled by
water at a temperature in the range of from 25 °C to
70 °C to yield the sulfuric acid ester of alcohol or its

25 ethoxylate. The sulfuric acid ester of the alcohol or its
ethoxylate then exits the falling film column and is
neutralized with an alkali metal solution, e.g., sodium
or potassium hydroxide, to form the alcohol sulfate salt
or the alcohol ethoxysulfate salt.

30   Suitable oxyalkylated alcohols can be prepared by
adding to the alcohol or mixture of alcohols to be oxy-
alkylated a calculated amount, e.g., from 0.1 to 0.6,

preferably from 0.1 to 0.4 percent by weight, based on
total alcohol, of a strong base, typically an alkali
metal or alkaline earth metal hydroxide such as sodium
hydroxide or potassium hydroxide, which serves as a
catalyst for oxlyalkylation. The resulting mixture is
dried, as by vapour phase removal of any water present,
and an amount of alkylene oxide calculated to provide
from about 1 mole to about 12 moles of alkylene oxide per
mole of alcohol is then introduced and the resulting
mixture is allowed to react until the alkylene oxide is
consumed, the course of the reaction being followed by
the decrease in reaction pressure.

The oxyalkylation is typically conducted at elevated
temperatures and pressures. Suitable reaction
temperatures range from 120 °C to 220 °C with the range
of from 140 °C to 160 °C being preferred. A suitable
reaction pressure is achieved by introducing to the
reaction vessel the required amount of alkylene oxide
which has a high vapour pressure at the desired reaction
temperature. For consideration of process safety, the
partial pressure of the alkylene oxide reactant is
preferably limited, for instance, to less than 512 kPa,
and/or the reactant is preferably diluted with an inert
gas such as nitrogen, for instance, to a vapour phase
concentration of about 50 percent or less. The reaction
can, however, be safely accomplished at greater alkylene
oxide concentration, greater total pressure and greater
partial pressure of alkyelene oxide if suitable pre-
cautions, known to the art, are taken to manage the risks
of explosion. With respect to ethylene oxide, a total
pressure of between about 376 and 858 kPa, with an
ethylene oxide partial pressure between 345 and 621 kPa,
is particularly preferred, while a total pressure of

between about 50 and 90 psig, with an ethylene oxide
partial pressure between 238 and 445 kPa, is considered
more preferred. The pressure serves as a measure of the
degree of the reaction and the reaction is considered to
be substantially complete when the pressure no longer
decreases with time.

It should be understood that the oxyalkylation
procedure serves to introduce a desired average number of
alkylene oxide units per mole of alcohol oxyalkylate. For
example, treatment of an alcohol mixture with 3 moles of
ethylene oxide per mole of alcohol serves to effect the
ethoxylation of each alcohol molecule with an average of
3 ethylene oxide moieties per mole alcohol moiety,
although a substantial proportion of alcohol moieties
will become combined with more than 3 ethylene oxide
moieties and an approximately equal proportion will have
become combined with less than 3. In a typical ethoxyla-
tion product mixture, there is also a minor proportion of
unreacted alcohol.

Other alkyene oxides can be used, such a proplyene
oxide and butylene oxide. These may be added as a
heteric mixture to the alcohol or sequentially to make a
block stucture.

The sulfated primary alcohol composition of the
invention can be used as surfactants in a wide variety of
applications, including detergents such as granular
laundry detergents, liquid laundry detergents, liquid
dishwashing detergents; and in miscellaneous formulations
such as general purpose cleaning agents, liquid soaps,
shampoos and liquid scouring agents.

The sulfated primary alcohol composition of the
invention find particular use in detergents, specifically
laundry detergents. These are generally comprised of a

number of components, besides the sulfated primary
alcohol composition of the invention:

    other surfactants of the ionic, nonionic, amphoteric
    or cationic type,

5   builders (phosphates, zeolites),cobuilders (poly-
    carboxylates),

    bleaching agents and their activators,

    foam controlling agents,

    enzymes,

10 anti-greying agents,

    optical brighteners, and

    stabilizers.

    Liquid laundry detergents generally comprise the same
    components as granular laundry detergents, but generally

15 contain less of the inorganic builder component. Hydro-
    tropes are often present in the liquid detergent formula-
    tions. General purpose cleaning agents may comprise other
    surfactants, builders, foam suppressing agents, hydro-
    tropes and solubilizer alcohols.

20 In addition to surfactants, washing and cleaning
    agents may contain a large amount of builder salts in
    amounts up to 90% by weight, preferably between 5-35% by
    weight, to intensify the cleaning action. Examples of
    common inorganic builders are phosphates, polyphosphates,

25 alkali metal carbonates, silicates and sulfates. Examples
    of organic builders are polycarboxylates, aminocarboxy-
    lates such as ethylenediaminotetraacetates, nitrilo-
    triacetates, hydroxycarboxylates, citrates, succinates
    and substituted and unsubstituted alkanedi- and poly-

30 carboxylic acids. Another type of builder, useful in
    granular laundry and built liquid laundry agents,
    includes various substantially water-insoluble materials
    which are capable of reducing the water hardness e.g. by

ion exchange processes. In particular the complex sodium
aluminosilicates, known as type A zeolites, are very
useful for this purpose.

5   The formulations may also contain percompounds with a
bleaching action, such as perborates, percarbonates,
persulfates and organic peroxy acids. Formulations con-
taining percompounds may also contain stabilizing agents,
such as magnesium silicate, sodium ethylenediaminetetra-
acetate or sodium salts of phosphonic acids. In addition,

10   bleach activators can be used to increase the efficiency
of the inorganic persalts at lower washing temperatures.
Particularly useful for this purpose are substituted
carboxylic acid amides, e.g., tetraacetylethylenedi-
amine., substituted carboxylic acids, e.g., isononyl-

15   oxybenzenesulfonate and sodiumcyanamide.

         Examples of suitable hydrotropic substances are
alkali metal salts of benzene, toluene and xylene
sulfonic acids; alkali metal salts of formic acid, citric
and succinic acid, alkali metal chlorides, urea, mono-,

20   di-, and triethanolamine. Examples of solubilizer
alcohols are ethanol, isopropanol, mono- or polyethylene
glycols, monopropylene glycol and etheralcohols.

         Examples of foam control agents are high molecular
weight fatty acid soaps, paraffinic hydrocarbons, and

25   silicon containing defoamers. In particular hydrophobic
silica particles are efficient foam control agents in
these laundry detergent formulations.

         Examples of known enzymes which are effective in
laundry detergent agents are protease, amylase and

30   lipase. Preference is given to the enzymes which have
their optimum performance at the design conditions of the
washing and cleaning agent.

A large number of fluorescent whiteners are described
in the literature. For laundry washing formulations, the
derivatives of diaminostilbene disulfonates and sub-
stituted distyrylbiphenyl are particularly suitable.

5   As antigreying agents, water soluble colloids of an
organic nature are preferably used. Examples are water
soluble polyanionic polymers such as polymers and copoly-
mers of acrylic and maleic acid, cellulose derivatives
such as carboxymethyl cellulose methyl- and hydroxyethyl-

10   cellulose.

In addition to one or more of the aforementioned
other surfactants and other detergent composition
components, compositions according to the invention
typically comprise one or more inert components. For

15   instance, the balance of liquid detergent composition is
typically an inert solvent or diluent, most commonly
water. Powdered or granular detergent compositions
typically contain quantities of inert filler or carrier
materials.

20   The following examples will illustrate the nature of
the invention.

Example 1

This example will demonstrate the manufacture of a
skeletally isomerized C_{16} olefin, subsequently converted

25   to a skeletally isomerized C_{17} primary alcohol composi-
tion according to the invention.

1 Litre of NEODENE 16 olefin, a C_{16} linear α-olefin
commercially available from Shell Chemical Company, was
first dried and purified through alumina. The olefin was

30   then passed through a tube furnace at about 250 °C set at
a feed rate of about 1.0 ml/minute and using a nitrogen
pad flowing at about 91 ml/minute. Working from the top,

the tube furnace was loaded with glass wool, then 10 ml
of silicon carbide, then the catalyst, followed by 5 ml
of silicon carbide, and more glass wool at the bottom.
The volume of the tube furnace was 66 ml. The reactor

5   tube furnace had three temperature zones, with a multi-
point thermocouple inserted into the tube reactor and
positioned such that the temperature above, below and at
three different places in the catalyst bed could be
monitored. The reactor was inverted and installed in the

10   furnace. All three zones, including the catalyst zone,
were kept at about 250 °C during the reaction and the
pressure was maintained in the reactor at 114 kPa.

The amount of catalyst used was 23.1g, or 53 ml by
volume. The type of catalyst used to structurally

15   isomerize the NEODENE 16 olefin was a 1.59 mm extruded
and calcined H-ferrierite containing 100 ppm palladium
metal.

This catalyst was prepared in accordance with
example C of USP 5,510,306, reproduced in part herein for

20   convenience. An ammonium-ferrierite having a molar
silica to alumina ratio of 62:1, a surface area of
369 square meters per gram (P/Po = 0.03), a soda content
of 480 ppm and n-hexane sorption capacity of 7.3 g per
100 g of zeolite was used as the starting zeolite. The

25   catalyst components were mulled using a Lancaster mix
muller. The mulled catalyst material was extruded using
an 25.4 mm or a 57.2 mm Bonnot pin barrel extruder.

The catalyst was prepared using 1 wt% acetic acid and
1 wt% citric acid. The Lancaster mix muller was loaded

30   with 645 grams of ammonium-ferrierite (5.4% Loss on
Ignition) and 91 grams of CATAPAL D alumina (LOI of
25.7%). The alumina was blended with the ferrierite for 5
minutes during which time 152 millilitres of de-ionized

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water was added. A mixture of 6.8 grams glacial acetic acid, 7.0 grams of citric acid and 152 milliliters of de-ionized water was added slowly to the muller in order to peptize the alumina. The mixture was mulled for

5   10 minutes. 0.20 Grams of tetraammine palladium nitrate in 153 grams of de-ionized water were then added slowly as the mixture was mulled for a period of 5 additional minutes. Ten grams of METHOCEL F4M hydroxypropyl methylcellulose was added and the zeolite/alumina mixture

10   was mulled for 15 additional minutes. The extrusion mix had an LOI of 43.5%. The 90:10 zeolite/alumina mixture was transferred to the 2.25 inch Bonnot extruder and extruded using a die plate with 1.59 mm holes.

       The moist extrudates were tray dried in an oven

15   heated to 150 °C for 2 hours, and then increased to 175 °C for 4 hours. After drying, the extrudates were longsbroken manually. The extrudates were calcined in flowing air at 500 °C for two hours.

       The olefin was passed through the reactor furnace

20   over a 5 hour period. Samples of 36.99 g and 185.38 g were collected at about the 1 and 5 hour point, and combined for a total of about 222 g. A portion of this sample was then vacuum distilled at 0.533 kPa to obtain a predominate amount of the C_{16} skeletally isomerized

25   olefin by collecting distillate cuts boiling at 160 °C in the pot and 85 °C at the head, and 182 °C in the pot and 75 °C at the head.

       A 90 Gram sample of the 110.93 grams of the skeletally isomerized olefin was then hydroformlyated

30   using the modified oxo process. 90 Grams of the skeletally isomerized olefin was reacted with hydrogen and carbon monoxide in about a 1.7:1 molar ratio in the

presence of a phosphine modified cobalt catalyst at a temperature of up to about 185 °C and a pressure of about 7684 kPa for four and one-half hours in a nitrogen purged 300cc autoclave. After completion of the reaction, the product was cooled to 60 °C.

5

40 Grams of the hydroformylated product was poured into a 100 ml flask and vacuum distilled for 4 hours at 0.533 kPa with temperature increases from start of 89 °C to a finish temperature of 165 °C. Distillate cuts of 20.14 g and 4.12 g were taken at 155 °C and 165 °C, respectively, and combined in a 100 ml flask.

10

To the distillate cuts in the flask was added 0.2 g of sodium borohydride, stirred, and heated up to 90 °C over an 8 hour period to deactivate the hydroformylation catalyst and stabilize the alcohols. The distilled alcohol was washed with 90 °C water three times, dried with sodium sulfate, and filtered into a 100 ml flask. The alcohol was then vacuum distilled for a further hour to distill off any remaining water. The product was then subjected to NMR analysis and sulfation to test for cold water solubility, detergency, and biodegradability.

15

20

Example 2

This example will demonstrate the manufacture of a skeletally isomerized C_{13-14} olefin, subsequently converted to a skeletally isomerized C_{14-15} primary alcohol composition according to the invention.

25

A C13-14 linear internal olefin having a composition of 53.38% linear C13 olefin, 45.24% of linear C14 olefin, 0.96% branched C13 olefin, and 0.29% branched C14 olefin, was subjected to skeletal isomerization using the same procedure and type of equipment as described above in example 1. The olefin was passed through the tube furnace

30

for 26 hours, except that after 8 hours the temperature of the tube furnace was increased in all three zones to 275 °C. At the 13 hours, 18 hours, 20 hours, and 26 hours mark, samples of the skeletally isomerized olefins were collected and combined for a total of 774 g.

Samples of gaseous and liquid products collected after 4.5 hours (at 250 °C) and 15.5 hours (at 275 °C) on stream were analyzed in order to determine their composition. At 250 °C, 70.1% of the C13 olefin feed was converted, and 75.6% of the C14 olefin feed was converted. At these conversion levels, the selectivity to branched C13 and C14 olefins was 96.3% and 97.8%, respectively. 67.4% of the C13 olefin feed was recovered as skeletally isomerized C13 branched olefin. 74.0% of the C14 olefin feed was recovered as skeletally isomerized C14 branched olefin.

At 275 °C, 79.4% of the C13 olefin feed was converted, and 82.2% of the C14 olefin feed was converted. At these conversion levels, the selectivity to branched C13 and C14 olefins was 91.5% and 92.1%, respectively. 72.6% of the C13 olefin feed was recovered as skeletally isomerized C13 branched olefin. 75.6% of the C14 olefin feed was recovered as skeletally isomerized C14 branched olefin.

The skeletally isomerized olefin was then vacuum distilled at 0.533 kPa. 636 Gram of distillate boiling in the pot at temperatures in the range of 135 °C to 145 °C and at the head within the range of 108 °C to 138 °C were collected.

606 Gram of the skeletally isomerized distilled olefin was hydroformylated by the above procedure, except in a 3.785 litre autoclave using a 37/63 mole% ratio of

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carbon monoxide to hydrogen for a period of 12-13 hours
at 4826 to 5516 kPa and 175 °C. 693 Gram of alcohol was
collected.

The alcohol was then flash distilled at 0.533 kPa to
collect the C_{14-15} alcohol, with about 650 g of dis-
tillate cut boiling in pot at 185 °C and at the head at
140 °C collected. This cut was treated with 5.0 g of
sodium borohydride, heated to about 100 °C, and then
treated with 5.0 more grams of sodium borohydride, for a
total heat time of 9 hours. The alcohol was washed with
90 °C water three times, dried with sodium sulfate,
filtered, and vacuum distilled at 0.533 kPa. Distillate
cuts boiling at 128 °C through 142 °C at the head were
collected and tested with NMR, after which they were
sulfated and tested for cold water solubility, deter-
gency, and biodegradability.

Example 3

The same procedure as used in example 1 was used to
skeletally isomerize a NEODENE 14 olefin commercially
available from Shell Chemical Company, which is a
C_{14} α-olefin, with subsequent conversion to a skeletally
isomerized C_{15} primary alcohol composition. The tube
furnace was kept at 250 °C. The skeletally isomerized
distillate cut boiling at 133 °C in the pot and 64 °C at
the head was collected and hydroformylated at
8963-9653 kPa for 5 hours at a molar ratio of H_2/CO of
1.7:1, using the equipment of example 1.

Example 4

The same procedure as used in example 1 was employed
to skeletally isomerize a NEODENE 12 olefin, a
C_{12} α-olefin, subsequently converted to a skeletally

isomerized C_{13} primary alcohol composition. The
skeletally isomerized olefin was vacuum distilled at
2.665 kPa, and the distillate cut boiling at 172 °C in
the pot and 105 °C at the head was collected and hydro-
formylated to an alcohol. The hydroformylation equipment
was as used in example 2, at 2032 kPa over an 8 hour
period, using a 37/63 mole% CO/H gas mixture. The
alcohol was vacuum distilled at 1.333 kPa, with those
cuts boiling at 141-152 °C in the pot and 127-132 °C at
the head being collected.

Example 5

The same olefin, procedure, and type of equipment as
used in example 2 was repeated. The C_{13-14} internal
olefin was skeletally isomerized at 250 °C. The iso-
merized olefin was vacuum distilled at 0.533 kPa, with
distillate cuts boiling at 95 °C and 77 °C at the head
being collected, as well as distillate cuts boiling
between 120 °C to 175 °C in the pot and 73 °C to 106 °C at
the head being collected under 2.665 kPa. The hydro-
formylation was conducted in an autoclave for about
9 hours at a pressure of 8032 kPa using a CO to H gas
ratio of 37/63 mole%. Afterwards, the distillate cut
boiling at 173 °C in the pot and 125 °C at the head was
collected and treated with sodium borohydride as in
example 2.

Example 6

Each of the primary alcohol compositions described in
examples 1-6 were sulfated by adding dropwise chloro-
sulfonic acid to the primary alcohol composition. Speci-
fically, the primary alcohol composition was sparged for
2-3 hours with nitrogen in a flask, after which about
1 ml of methylene chloride per gram of the primary

alcohol composition was added. The chlorosulfonic acid was added dropwise to the primary alcohol composition in the flask for about 25 minutes, while maintaining the temperature at about 30-35 °C. More methylene chloride

5   was added if the solution became to viscous. The solution was then sparged with nitrogen for 2-3 minutes to facilitated removal of HCl, after which it was added slowly to a chilled 50% sodium hydroxide in 3A alcohol solution to neutralize the primary alcohol composition.

10   If the pH was below 8, more of the basic solution was added, until the pH was adjusted to between 8-9. If too acidic, a 50% solution of H_2SO_4 was added to adjust the pH. The solution was stirred for another hour, and the pH adjusted accordingly within the stated range. Methylene

15   chloride was removed by a rotary evaporator under reduced pressure at about 40 °C under a nitrogen sparge.

     The primary alcohol compositions were subsequently tested for amount, type, and location of branching using the JSME NMR method described herein. For a deter-

20   mination of quaternary carbon atoms, the quat only JSME NMR technique described herein was used. These results are reported in Table 1 below. The sulfated primary alcohol samples were also tested for biodegradability, the results of which are reported in

25   Table II; and detergency, the results of which are reported in Table III. The examples reported in the tables are arranged by order of chain length for ease of viewing, and identified as 6- indicating the sulfate of a corresponding example number. Each of these tests were

30   conducted in accordance with the procedures specified above. As a comparison example, NEODOL 45-Sulfate was tested for branching, biodegradability, and detergency.

NEODOL 45-S was used as the comparison because it is the current commercial primary alcohol composition, which when sulfated, is currently used in detergents and is known for its ready biodegradability.

Table I

NMR Structural Characterization

Analysis	Ex 4, a C13 alcohol	Ex 2, a C14-15 alcohol	Ex 3, a C15 alcohol	Ex 1, a C17 alcohol	NEODOL 45, a C14-15 alcohol
Average Carbon Number	13.9	15.1	15.0	17.0	14.7
Average Branches per Chain	1.3	1.6	1.3	1.6	0.3
Branch Position Relative To Hydroxyl Carbon					
% at C4 position and further, including no branching	70.2	67.1	65.1	67.9	81.5
% at C3 position	20.6	20.5	19.6	21.0	0.0
% methyl at C2 position	4.7	5.9	5.2	4.0	7.4
% ethyl at C2 position	1.0	1.3	2.3	1.2	2.7
% propyl and longer at C2 position	3.5	5.3	7.8	5.9	8.4

Table I (cont'd)

NMR Structural Characterization

Analysis	Ex 4, a C$_{13}$ alcohol	Ex 2, a C$_{14-15}$ alcohol	Ex 3, a C$_{15}$ alcohol	Ex 1, a C$_{17}$ alcohol	NEODOL 45, a C$_{14-15}$ alcohol
Types Of Branching					
% Propyl and longer	38	32.5	37.6	41.7	88.8
% ethyl	10.8	12.5	12.8	16.3	3.1
% methyl	38.2	38.9	38.3	42.0	8.1
% isopropyl termination	13.0	16.1	11.3	0.0	0.0
% Linear Alcohol (By GC)	na	<2%	na	<1%	78%
Quaternary Carbons Detected	none	none	not analyzed	none	none

The results above indicate that the skeletally
isomerized branched alcohols according to the invention
have a very high average number of branches per molecule
chain, well exceeding 0.7, while the commercial NEODOL 45
has an average number of branches which is quite low, on
the order of 0.3. The patterns of branching are
strikingly similar for the different alcohols according
to the invention except that the branched C_{17} is
curiously deficient in isopropyl termination. The results
also indicate a sharp increase in the number of branches
occurring at the C_3 position compared to the lack of any
branches in the NEODOL 45 alcohol at the C_3 position. Of
the types of branches detected, most of the branches are
methyl groups for both the skeletally isomerized alco-
hols and the NEODOL alcohol. However, the skeletally
isomerized alcohol methyl branches are not concentrated
at the C_2 position, as is the case for NEODOL 45 and
other conventional detergent range alcohols. A further
distinguishing feature of the skeletally isomerized
alcohols is that they contain a larger proportion of
ethyl types of branches than the NEODOL 45. Further,
except the C_{17} branched alcohol, most of the embodiments
were also skeletally isomerized at the terminal part of
the hydrophobe, as indicated by the high percentage of
terminal isopropyl formation, in contrast to none found
in the NEODOL 45.

The results also support a conclusions that a pre-
dominate number of branches in the skeletally isomerized
alcohols are concentrated towards the ends of the mole-
cule chain, i.e., at the C_2, C_3, and at the isopropyl
terminal position, rather than towards the center of the
molecule chain. NMR data showing a high percentage of

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methyl, ethyl, and isopropyl branching for a compound
whose branching is predominately towards the center of
the chain, i.e. inward from the fourth carbon on either
end of the chain, typically have very low percentages of
branching at the C_2 and C_3 positions. The data above,
however, shows both a high percentage of methyl, ethyl,
and isopropyl types of branches as well as a high amount
of branching occurring at the C_2 and C_3 positions,
indicating that the molecule has a higher concentration
of branches at the C_2 and C_3 carbon positions at the ends
of the carbon chain than the number of branches found at
the C_4 or longer positions from both ends of the molecule
proceeding inward towards the center.

Finally, in spite of the high number of branches per
molecule chain, no quaternary carbon atoms were detected
by the modified NMR JSME method. This would suggest
that these compounds should readily biodegrade.

Table II

% Biodegradation of Skeletally Isomerized Alcohol
Sulfates

Example No.	5-day	10-day	15-day	28-day
6-4, a C_{13} alcohol sulfate	47	61	71	100
6-2, a C_{14-15} alcohol sulfate	38	58	65	100
6-3, a C_{15} alcohol sulfate	22	48	63	69
6-1, a C_{17} alcohol sulfate	44	56	70	89
A sulfated NEODOL C_{14-15} alcohol	44	63	78	86

    The OECD 301D biodegradation results indicate that
each of the sulfated primary alcohol compositions of the
invention readily biodegraded. Some of the sulfated
primary alcohol compositions of the invention even

5   exhibited 100% biodegradation at 28 days.

Table III

Multisebum Detergencies of Skeletally Isomerized Alcohol Sulfates

Example No.	10 °C	32 °C
6-4, a C_{13} alcohol sulfate	12	14
6-2, a C_{14-15} alcohol sulfate	37	49
6-3, a C_{15} alcohol sulfate	39	50
6-1, a C_{17} alcohol sulfate	24	35
A sulfated NEODOL C_{14-15} alcohol	16	34

LSD_{95} (Least Significant Difference at 95% probability) is 5.0 at both temperatures.

The detergency results indicate that the alcohol sulfate compositions of the invention exhibited extremely good cold water detergency. For example, 6-2 far out-performed the sulfated NEODOL alcohol, each of equal chain length, in both cold and warm water detergency. A composition having good cold water detergency is one in which has superior cold water detergency over a sulfated NEODOL alcohol of the same chain length. Preferred, however, are those alcohol sulfates which have a cold water detergency of 22% or more, most preferably 28% or more.

Example 7

This example demonstrates the manufacture of a dimerized monobranched $C_{12}-C_{15}$ alcohol from internal olefins using a nickel chelate catalyst.

A flask was charged with 2268.7 grams of a composition of C_6-C_8 internal olefins containing some 4, 5, 9, and 10 carbon olefins, and distilled using an 11 plate Oldershaw distillation column with a swinging bucket

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reflux splitter condensor, a dry ice chilled trap, and a
nitrogen blanket. After 37 hours of distillation, those
cuts distilling up to 138 °C in the pot and 125 °C at the
head were collected for a total amount of about

5   1200 grams. These cuts represent the light ends of the
olefin, C_{4-8}.

The 1200 grams of the C_{4-8} olefin feed was dimerized
by the following method. The 1200 grams of the olefin
was poured into a 5 litre round bottom flask equipped

10   with a condensor, a dry ice condensor, a thermocouple, a
water bath, and a nitrogen blanket. 19.74 Gram of dried
nickel hexafluoroacetoacetyl acetonate (nickel catalyst)
and 53.76 g of an 11/89 wt.% solution of diethylaluminium
ethoxide in cyclohexane (aluminium solution) were added

15   sequentially and stirred into the olefin. The reaction
mixture was heated up to 35 °C for 6.5 hours, after which
14.38 more grams of the aluminium solution were added,
heated up to 37 °C for an additional 2 hours, after which
4.0 more grams of the nickel catalyst and 13.75 g of the

20   aluminium solution were added, heated up to 35 °C to
37 °C for another 10 hours, after which 15.55 more grams
of the aluminium solution were added followed by heating
for another 4 hours, after which 4 more grams of the
nickel catalyst and 14.4 more grams of the aluminium

25   solution were added, followed by heating for another
5 hours, after which 21.0 more grams of the aluminium
solution and 5.0 grams of the nickel catalyst were added,
followed by heating for another 3 hours, after which
4.18 grams of the nickel catalyst and 20.1 more grams of

30   the aluminium solution were added.

Subsequently, the reaction product in the flask was
quenched with 100 g of citric acid and 22 g of a sodium

bicarbonate solution per 0.946 litre (quart) of water,
and filtered.

The dimerized C$_{4-8}$ olefin was then subjected to
further distillation to obtain cuts having predominantly
C$_{13-14}$ olefins. The distillation was conducted as above,
except with a 10 plate Oddershaw column, and those cuts
distilling at 169 °C to 194 °C in the pot and 129 °C to
155 °C at the head, at 6.3-6.4 kPa vacuum, were col-
lected, for a total of 188.05 grams.

150 grams of this batch was then subjected to hydro-
formylation in a 500 ml autoclave, using the modified oxo
process. The 150 grams of the dimerized olefin were
reacted with hydrogen and carbon monoxide at a H$_2$/CO
ratio of 2, in the presence of a phosphine modified
cobalt catalyst and potassium hydroxide in ethanol at a
temperature of up to 180 °C, a stirring speed of
1250 rpm, and a pressure of 6894 kPa, for 20 hours.
After completion of the reaction, the product was cooled
to 60 °C.

The hydroformylated dimerized alcohols were subjected
to further flash volatilization do separate out any
unconverted olefin and paraffins. Those cuts distilling
at 182 °C to 250 °C in the pot and 99 °C to 112 °C at the
head were collected, and neutralized with sodium boro-
hydride. The distillate cuts, totaling 300 ml, were added
to a round bottom flask, stirred and heated to 50 °C, to
which 0.6 grams of the sodium borohydride were added and
reacted for about 2 hours, after which 0.6 more grams of
the sodium borohydride were added and reacted for another
1.5 hours at 75-80 °C, and then reacted for another 2 and
1/2 hours at 98-100 °C. The solution was left to cool,

transferred to a 500 ml flask, washed by shaking with
70 °C deionized water under ventilation, let stand, to
which was added 20 ml of ethyl ether, shaken, and
separated. The water phase was drained and the process
5   repeated another two times using ethyl ether. After
washing, 10 grams of sodium sulfate was added to the
alcohol, shook, and then let stand. The product was
filtered, the liquid transferred to a 250 ml flask, and
then subjected to further distillation to rid the solu-
10   tion of the light ends. The distillates obtained up to
102 °C in the pot and 163 °C at the head were discarded,
and 82.91 ml of the contents in the pot were recovered.
These contents were monobranched C_{12-16} alcohols, having
42% C_{14}, 44% C_{15}, and 8% C_{16} alcohols as determined by
15   GCMS, and were subjected to analytical testing and
further reaction for making the sulfates.

Example 8

This example demonstrates the preparation of a C_{13-17}
dimerized monobranched alcohol from internal olefins
20   using a nickel carboxylate catalyst.

The same procedure as used in Example 1 above was
followed with the following noted exceptions. The amount
of C_{4-10} internal olefins distilled was 2427.7 grams.
712.5 grams of distillate boiling at 120 to 154 °C in the
25   pot and 89 °C to 129 °C at the head were collected. The
reflux was set at 5 seconds on, and 7 seconds off. The
distillate cuts were predominantly C_{6-9} carbon chain
internal olefins. 702.6 grams of these olefins were
dimerized in a 2 litre flask using 0.493 g of nickel
30   2-ethylhexanoate-tirfluoroacetate in 5 ml of cyclohexane
and 12 ml of a 1 molar solution of ethylaluminium di-
chloride in hexane, (first batch of catalyst) as the

dimerization catalysts injected into the olefin. The
contents of the flask were heated to 35-38 °C on average
throughout the course of the reaction. After about
3 hours of heat, a second batch catalyst in the same
amount was added. After another hour of heat, a third
batch of catalyst in the same amount was added, and after
another hour and 15 minutes, a fourth batch of catalyst
in the same amount was added. After 6.5 hours, the fifth
batch of catalyst in the same amount was added, and after
another 7 hours of heat, another catalyst batch in the
same amount was added, and finally after another
1.5 hours, the final catalyst batch in the same amount
was added. The contents of the flask were heated for
another hour.

To neutralize the dimerization catalyst, 22 g of
sodium bicarbonate in 250 g of deionized water was added
to 100 g of citric acid in 100 grams of deionized water,
to which was added more water to make a 1 litre batch.
The dimerized olefins were poured into a 2 litre separa-
tion funnel with 1/2 litre of the citric acid/bicarbonate
solution, shook and vented, separated, and repeated. The
neutralized dimerized solution was dried with sodium
sulfate as above.

As in example 1, the olefins were further distilled
to acquire C_{6-9} olefins. Those distillate cuts boiling
at 157 °C in the pot and 125 °C at the head at 5.5 kPa,
and those boiling at 139 °C to 164 °C in the pot at
1.866 kPa, and those boiling at from 179 °C to 240 °C in
the pot at 1.9 kPa were collected for a total of
231.95 grams of distillate.

The dimerized distillate was hydroformylated as above
and flash distilled at about 0.5-0.7 kPa. 1.39 Gram of

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sodium borohydride was added to 211.48 g of the distilled
alcohol, heated to 50 °C for 1 hour, after which another
1.3 g of sodium borohydride was added and heated to 90 °C
for four hours and cooled.

5   The product was washed as above, and redistilled with
those distillate cuts boiling at 141.5 to 240 °C in the
pot and 100 °C to 104 °C at the head being collected at
0.4 kPa. The monobranched C_{13-17} alcohols, having 25%
C_{14}, 40% C_{15}, and 25% C_{16} alcohols, as determined by
10   GCMS, were collected and subjected to analytical testing
and sulfation as described below.

Example 9

This example demonstrates the preparation of a
$C_{13,15,17}$ dimerized monobranched alcohols from alpha
15   olefins.

In this example, a mixture of 600g NEODENE
6 α-olefin, a C_6 olefin, and 800 g of NEODENE
8 α-olefin, a C_8 olefin, containing 5.32 g of ethyl-
aluminium dichloride, were added to a 5 litre flask. The
20   same procedure as used in example 1 was followed with the
following differences. A solution of 7.9 g of the nickel
2-ethylhexanoate-tirfluoroacetate in 6.35 g of cyclo-
hexane (the nickel solution) was added and heated. The
flask was maintained at from 33 °C to 38 °C throughout
25   the course of the reaction. Another 7.6 ml of the alu-
minium solution as prepared in example 2 and 5 ml of the
nickel solution were injected into the reaction flask
after about 8 hours of heating.

1.5 Litres of the sodium citrate neutralizing
30   solution was used to neutralize the dimerized olefins,
separated, and again repeated. The dimerized product was

distilled, with the cuts distilling at 149 °C to 160 °C
in the pot and 137 °C to 148 °C at the head, at 8.0 kPa,
120 °C to 133 °C in the pot and 110 to 122 °C at the head
at 1.2 kPa, and 127 to 149 °C in the pot and 118 °C to
145 °C at the head at 1.3 kPa being collected for a total
of 786.4 g.

730 G of these dimerized olefins were hydroformylated
in a 3.785 litre autoclave, reacted at temperatures up to
240 °C at pressures up to 7894 kPa.

809 G of the hydroformylated olefins were treated
with 6.5 g of sodium borohydride, as above, followed by
another addition of 6.5 g of sodium borohydride and
heating, and a third addition of 4.95 g followed by
6 hours of heating at up to 99 °C.

The treated hydroformylated olefins were washed as in
example 1, filtered, and distilled with those cuts dis-
tilling at 152 to 181 °C in the pot and 137 to 172 °C at
the head at 0.8 kPa being collected for a total of 495 g
of C_{13}, C_{15}, and C_{17} monobranched alcohols. The sample
was analytically tested and sulfated as described below.
Example 10

Each of the monobranched alcohol compositions des-
cribed in examples 7-9 were sulfated by adding dropwise
chlorosulfonic acid to the alcohol composition. Speci-
fically, the alcohol compositions were sparged for
2-3 hours with nitrogen in a flask, after which about
1 ml of methylene chloride per gram of the alcohol
composition was added. The chlorosulfonic acid was added
dropwise to the alcohol composition in the flask for
about 25 minutes, while maintaining the temperature at
30-35 °C. More methylene chloride was added if the
solution became to viscous. The solution was then

sparged with nitrogen for 2-3 minutes to facilitate
removal of HCl, after which it was added slowly to a
chilled 50% sodium hydroxide in 3A alcohol solution to
neutralize the alcohol composition. If the pH was below
5   8, more of the basic solution was added, until the pH was
adjusted to between 8-9. If too acidic, a 50% solution of
H_2SO_4 was added to adjust the pH. The solution was
stirred for another hour, and the pH adjusted accordingly
within the stated range. Methylene chloride was removed
10   by a rotary evaporator under reduced pressure at 40 °C
under a nitrogen sparge.

        The alcohol compositions of examples 1-3 were sub-
sequently tested for amount, type, and location of
branching using the JSME NMR method described herein.
15   For a determination of quaternary carbon atoms, the quat
only JSME NMR technique described herein was used. These
results are reported in Table 1 below. The average carbon
number was determined by GCMS. The sulfated primary
alcohol samples were also tested for biodegradability,
20   the results of which are reported in Table II; and deter-
gency, the results of which are reported in Table III.
The examples reported in the tables are arranged by order
of chain length for ease of viewing, and identified as
10- indicating the sulfate of a corresponding example
25   number. Each of these tests were conducted in accordance
with the procedures specified above. As a comparison
example, NEODOL 45-Sulfate was tested for branching,
biodegradability, and detergency. NEODOL 45-S was used as
the comparison because it is the current commercial
30   primary alcohol composition, which when sulfated, is
currently used in detergents and is known for its ready
biodegradability. Also as a comparison, a sulfated

EXXAL-13S alcohol believed to have a predominance of C_{13} alcohols and derived from propylene oligomerization through acid catalysis and then subjected to hydro-formylation using an oxo process, was subjected to biodegradation testing. EXXAL 13 is reported to have about 3-4 methyl branches per tridecyl-alcohol molecule.

Table IV

NMR Structural Characterization

Analysis	Ex 7, a C_{12-15} alcohol	Ex 8, a C_{13-15} alcohol*	Ex 9, a $C_{13,15,17}$ alcohol	NEODOL 45, a C_{14-15} alcohol
Average Carbon Number	14.5	15.5	16.8	14.7
Average Branches per Chain	1.0	1.4	1.5	0.3
Branch Position Relative To Hydroxyl Carbon				
%@ C4 position and further, including no branching	83.7	85	83.4	81.5
%@ C3 position	4.7	3	2.7	0.0
% methyl @ C2 position	6.4	6	7.4	7.4
% ethyl @ C2 position	1.6	2	6	2.7
% propyl and longer @ C2 position	3.6	4	4.1	8.4

Table IV (con'd)

NMR Structural Characterization

Analysis	Ex 7, a C_{12-15} alcohol	Ex 8, a C_{13-15} alcohol*	Ex 9, a $C_{13,15,17}$ alcohol	NEODOL 45, a C_{14-15} alcohol
Types Of Branching				
% Butyl or longer	52.2	28		
% Propyl	17.5	12	66.7**	88.8**
% ethyl	16	23	12.9	3.1
% methyl	14.2	37	20.4	8.1
Quaternary Carbons Detected	na	none	na	none

* Approximately 21% of the branching was conjugated with
  methyl branches on adjacent carbons in the chain.
**Includes propyl and butyl branching.

   The results indicate that the dimerized alcohols
according to the invention look very much the same as
NEODOL alcohols with respect to the branch positions,
according to the NMR analysis. Specifically, very few
branches are located at the C_{2-4} carbon positions. Since
the average number of branches of the dimerized alcohols
far exceeds that of NEODOL alcohols, the center of the
molecule carbon backbone must be where the predominant
number of branches are situated, i.e. an excess of 80%.
By center is meant the C_4 position inward from each end
of the molecule.

   Also noteworthy is the higher percentage of ethyl
branches on the dimerized alcohols of the invention as

compared to the relatively few ethyl branches found in
the NEODOL alcohol.

Table V

% Biodegradation of Dimerized Alcohol Sulfates

Example No.	5-day	10-day	15-day	28-day
10-7	19	43	61	68
10-8	23	39	65	73
10-9	28	35	60	64
A sulfated NEODOL C_{14-15} alcohol	40	64	71	75
A sulfated EXXAL 13-S	4	12	21	40

The OECD 301D biodegradation results indicate that
each of the sulfated primary alcohol compositions of the
invention biodegraded readily, as did the NEODOL sulfated
alcohol. The sulfated EXXAL alcohol biodegraded only
poorly.

Table VI

Multisebum Detergencies of Dimerized Alcohol Sulfates

Example No.	10 °C	32 °C
10-7	27	31
10-8	21	31
10-9	15	25
A sulfated NEODOL C_{14-15} alcohol	11	29

LSD_{95} (Least Significant Difference at 95% probability)
is 5.0 at both temperatures.

The detergency evaluations indicate that the
dimerized alcohols of the invention have superior or
equal cold water detergency as compared to the con-
ventional NEODOL sulfated alcohol.

C L A I M S

1. A branched primary alcohol composition, having from 8
to 36 carbon atoms and an average number of branches per
molecule of from 0.7 to 3.0, said branching comprising
methyl and ethyl branches.

5   2. A branched primary alcohol according to claim 1,
wherein the average number of branches per molecule
ranges from 1.0 to 3.0.

3. A branched primary alcohol composition according to
claim 1 or 3, wherein the average number of branches per
10   molecule ranges from 1.5 to 2.3.

4. A branched primary alcohol composition according to
any one of claims 1 to 3, comprising less than 0.5 atom %
of quaternary carbon atoms.

5. A branched primary alcohol composition according to
15   any one of claims 1 to 4, containing less than 5% of
linear alcohols.

6. A branched composition according to any one of claims
1 to 5, wherein at least 40% of the number of branches in
the alcohol are methyl branches.

20   7. A branched alcohol composition according to any one
of claims 1 to 6, wherein from 5% to 30% of the number of
branches in the alcohol are ethyl branches.

8. A process for preparing a branched primary alcohol
composition according to claim 1, which process comprises
25   the steps of:

a) contacting an olefin feed comprising a linear olefins
having at least 7 carbon atoms with a catalyst effective
for skeletally isomerising said linear olefin to yield a
branched olefin of the same carbon number; and

b) converting said branched olefin to said primary alcohol composition.

9. A process according to claim 8, wherein the skeletally isomerising catalyst comprises a molecular sieve having at least one channel with a crystallographic free diameter along the x and/or y planes of the [001] view ranging from 0.42 to 0.70 nanometer, the molecular sieve preferably being a zeolite having the ferrierite isotypic structure.

10. A process for preparing a branched primary alcohol composition according to claim 1, having from 13 to 21 carbon atoms, which process comprises the steps of:

a) dimerising, in the presence of a homogeneous di- merisation catalyst, an olefin feed comprising a C_6-C_{10} olefin to yield a $C_{12}-C_{20}$ branched olefin; and

b) Converting said $C_{12}-C_{20}$ branched olefin to said branched primary alcohol composition.

11. A process according to claim 10, wherein the olefin feed comprises at least 90% of linear olefins.

12. A process according to claim 10 or 11, wherein the olefin feed comprises at least 50% of internal olefins.

13. A process according to any one of claims 10 to 12, wherein said dimerisation catalyst comprises a com- bination of a nickel carboxylate with an alkyl aluminium halide, or a combination of a nickel chelate with an alkyl aluminium alkoxide.

14. A process according to any one of claims 8 to 13, wherein the conversion of the olefin to the alcohol in step b) is effected by hydroformylating the olefin with carbon monoxide and hydrogen, in the presence of a hydro- formylating catalyst.

15. A branched primary alcohol alkoxylate composition, preparable by reacting a branched primary alcohol compo-

sition according to any one of claims 1 to 7 with an
oxirane compound.

16. A branched primary alcohol alkoxylate composition
according to claim 15 wherein the alkoxylate is pre-
dominantly ethoxylate, preparable by reacting the primary
alcohol composition with ethylene oxide.

17. A branched primary alkyl sulphate, preparable by
sulfating a primary alcohol composition according to any
one of claims 1 to 7.

18. A branched alkoxylated primary alkyl sulphate,
preparable by alkoxylating and sulphating a branched
primary alcohol composition according to any one of
claims 1 to 7.

19. A branched primary alkyl carboxylate, preparable by
oxidising a branched primary alcohol composition
according to any one of claims 1 to 7.

20. A detergent composition comprising:

a)   one or more surfactant(s) selected from the group of
branched primary alcohol alkoxylates according to
claim 15, branched primary alkyl sulphates according to
claim 17, and branched alkoxylated primary alkyl sul-
phates according to claim 18;

b)   a builder; and

c)   optionally one or more additives selected from the
group of foam controlling agents, enzymes, bleaching
agents, bleach activators, optical brighteners, co-
builders, hydrotropes and stabilisers.

21. A detergent composition according to claim 20,
wherein the builder is chosen from the group of alkali
metal carbonates, silicates, sulphates, polycarboxylates,
aminocarboxylates, nitrilotriacetates, hydroxycarboxy-
lates, citrates, succinates, substituted and unsub-

stituted alkane-di- and poly-carboxylic acids, complex
aluminosilicates, and mixtures thereof.

22. A detergent composition according to claim 20 or 21,
containing a bleaching agent which is selected from the
group of perborates, percarbonates, persulfates, organic
peroxy acids, and mixtures thereof.

23. A detergent composition according to any one of
claims 20 to 22, containing a bleach activator which is
selected from the group of carboxylic acid amides,
substituted carboxylic acids, and mixtures thereof.

24. A detergent composition according to any one of
claims 20 to 23, containing a hydrotrope which is
selected from the group of alkali metal salts of aromatic
acids or alkyl carboxylic acids, alkali metal chlorides,
urea, mono- or polyalkanolamines, and mixtures thereof.

25. A detergent composition according to any one of
claims 20 to 24, which is chosen from the group of
granular laundry detergents, liquid laundry detergents,
dishwashing detergents, soaps, shampoos, and scouring
detergents.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 97/06694

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6   C07C31/125   C07C43/13   C07C305/06   C07C53/126   C11D1/72
          C11D1/14   C11D1/29

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6   C07C   C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	FR 1 151 630 A (IMPERIAL CHEMICAL INDUSTRIES) 3 February 1958 see the whole document ---	1-14
A	WO 85 02175 A (MONSANTO CO) 23 May 1985 see claims -----	1-25

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
28 April 1998	07/05/1998

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl. Fax: (+31-70) 340-3016	Van Geyt, J

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INTERNATIONAL SEARCH REPORT

Information on patent family members

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
FR 1151630 A	03-02-58	NONE	
WO 8502175 A	23-05-85	EP 0161251 A	21-11-85